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LONG-TERM APPLICATIONS OF NITROGENOUS FERTILIZERS
ON A SOLONETZIC SOIL AND THEIR EFFECTS ON PLANT GROWTH
AND SOIL PROPERTIES

by



KENNETH JOHN PERL

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "Long-term applications of nitrogenous fertilizers on a Solonetzic soil and their effects on plant growth and soil properties" submitted by Kenneth John Perl, in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

Two field trials on the Solonetzic Soil Research Substation at Vegreville, Alberta, were established to investigate the ameliorative effects of N fertilizer applications on a Solonetzic Duagh SiL. Treatments in one trial included NH_4NO_3 , NH_2CONH_2 and $(\text{NH}_4)_2\text{SO}_4$ each applied at an annual rate of 112 kg/ha N for 10 years. In the other experiment, NH_4NO_3 was applied at 300 kg/ha N annually for 12 years. In both field trials, brome grass yields increased dramatically; Na and Ca were leached from the surface horizon and soil acidification increased substantially.

The foregoing observations prompted a detailed study of the effects of the long-term fertilizer treatments on the chemical properties of the soils. In addition, a greenhouse study determined the yield and chemical composition of barley plants grown on the $(\text{NH}_4)_2\text{SO}_4$ treated field soil compared to plants grown on the Check soil which received no N fertilizer treatment in the field.

Chemical analyses of samples from selected profile depths revealed that N fertilizers had acidified the Ap horizon, and to a lesser extent the upper Bnt. $(\text{NH}_4)_2\text{SO}_4$ was the most dramatic treatment followed by NH_4NO_3 , then NH_2CONH_2 . Also, mainly within the Ap horizon; Na, Ca and Mg contents were lowered while NH_4OAc -extractable Al and Mn increased, with $(\text{NH}_4)_2\text{SO}_4$ causing the most noticeable effects. The applications of NH_4NO_3 at 300 kg/ha N per year over

12 years decreased pH from 6.2 to 4.7 in the Ap horizon, lowered Na, Ca, K and Mg and increased Mn and Al levels. These changes were comparable to the lower rate of $(\text{NH}_4)_2\text{SO}_4$ in the other experiment. NH_4NO_3 at a high rate improved the Ca:Na ratio in the Ap horizon while it and $(\text{NH}_4)_2\text{SO}_4$ had a beneficial effect of increasing the Ca:Na ratio of the Bnt. In time this should lead to solodization of the Solonetz soil. However, both fertilizer treatments had a deleterious effect by acidifying the soil to an undesirable extent. In the greenhouse experiment, barley grown in the acidified $(\text{NH}_4)_2\text{SO}_4$ field soil generally had lower Na, Ca and Mg contents, markedly higher Al and Mn contents and significantly lower yields than plants grown in the Check field soil. Yields were improved and levels of plant Al and Mn decreased by liming the acid soil suggesting that low pH and related Al and Mn toxicities were responsible for the reduced growth. Applications of $\text{Ca}(\text{NO}_3)_2$ in the greenhouse reduced the Al content of barley plants and gave the greatest response of all the treatments; yet pH of the acidic soil was not adjusted upward nor were Mn contents in the plants lowered. This suggests the $\text{Ca}(\text{NO}_3)_2$ reduced Al uptake and perhaps had a physiological effect on the plant that enabled it to tolerate the Mn levels. Annual crops drilled directly into the Ap would be most susceptible to acid soil conditions. It would seem desirable that liming to control pH and provide Ca enrichment should complement applications of N fertilizers on Solonetzic soils.

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
LITERATURE REVIEW.	3
MATERIAL AND METHODS	32
Description of Field Soils Sampled.	32
Sampling of Field Soils for Laboratory Analysis	33
Preparation of Soil Samples for Laboratory Analysis	33
Field Soil Sampling and Preparation for Greenhouse Study.	34
Laboratory Analysis: Soils	34
Greenhouse Study.	36
Statistical Analysis of Data.	40
RESULTS AND DISCUSSION	41
Soil Analysis Data from the "Various Forms of N Trial".	41
Introduction	41
Cation Exchange Capacity (CEC)	42
Electrical Conductivity (EC)	42
Exchange acidity	43
Soil pH.	43
Extractable Al	45
Soil Mn.	45
Soil K	46

	<u>Page</u>
Soil Na.	46
Soil Ca.	47
Extractable Ca:Na ratio.	48
Soil Mg.	48
High Rates of NH_4NO_3 vs. Check Field Experiment: Soil	
Analysis Data	49
Introduction	49
Cation exchange capacity	67
Electrical conductivity.	67
Soil reaction.	67
Exchange acidity	67
Extractable Al	68
Soil Mn.	68
Soil K	68
Soil Na.	69
Soil Ca.	69
Extractable Ca:Na ratio.	70
Soil Mg.	70
Summary of soil analyses	71
Greenhouse Data	76
Introduction	76

	<u>Page</u>
Soil pH.	77
Dry matter yield of barley	78
Barley uptake of Al.	81
Barley uptake of Mn.	82
Barley uptake of Na.	82
Barley uptake of Ca.	83
Ca:Na ratio within barley tissues.	84
Barley uptake of Mg.	84
Barley uptake of K	84
Summary of results from greenhouse trial	85
GENERAL CONCLUSIONS.	92
LITERATURE CITED	98
APPENDIX	106
A. Experimental field design: Various forms of N: Duagh SiL	106
B. Plot diagram: Fertility test: Duagh SiL	107
C. Soil pH after cropping, dry matter yield and chemical composition of barley plants grown on the Ap horizon of a Duagh SiL Check and a Duagh Ap that received long-term treatments of $(\text{NH}_4)_2\text{SO}_4$ at a rate of 112 kg/ha N per year in the field prior to greenhouse experiment ($p \leq 0.05$).	108

LIST OF TABLES

	<u>Page</u>
Table 1. Greenhouse treatments applied to the Ap horizon of a Duagh SiL that received long-term repeated applications of $(\text{NH}_4)_2\text{SO}_4$ in the field and to the Ap horizon of a Duagh SiL Check	37
Table 2. Chemistry of a Duagh SiL: various forms of N applied: cation exchange capacity; electrical conductivity; exchange acidity; and soluble Mn at several fixed profile depths	50
Table 3. Chemistry of a Duagh SiL: various forms of N applied: pH; extractable Al, Mn and K at several fixed profile depths.	52
Table 4. Correlation of specific soil parameters including pH and extractable cations for various forms of N applied to a Duagh SiL	54
Table 5. Chemistry of a Duagh SiL: various forms of N applied; soluble Na, Ca, Mg and K at several fixed profile depths.	55
Table 6. Chemistry of a Duagh SiL: various forms of N applied; extractable Na, Ca, Mg and Ca:Na ratios at several fixed profile depths.	57
Table 7. Soil analysis for a Duagh SiL receiving long-term applications of a high rate of NH_4NO_3 vs. Check	72
Table 8. Soil analysis for a Duagh SiL receiving long-term repeated applications of NH_4NO_3 vs. Check; soluble cations.	73
Table 9. Correlation of pH and extractable cations for Check vs. NH_4NO_3 applied at 300 kg/ha N annually for 12 years on a Duagh SiL	74
Table 10. Soil pH after cropping, dry matter and chemical composition of barley plants grown on the Ap horizon of a Duagh SiL Check and a Duagh Ap that received long-term treatments of $(\text{NH}_4)_2\text{SO}_4$ at a rate of 112 kg/ha N per year in the field prior to greenhouse experiment.	87

Table 11. Correlation of soil pH after cropping, yield and chemical composition data of barley plants grown in the greenhouse on the Ap horizon of a Duagh SiL Check and a Duagh Ap receiving long-term treatments of $(\text{NH}_4)_2\text{SO}_4$ at a rate of 112 kg/ha N per year.	89
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LIST OF FIGURES

	<u>Page</u>
Figure 1. Effects of several N fertilizers on soil pH of Ap and Bnt horizons of a Duagh SiL	59
Figure 2. Effects of several N fertilizers on exchange acidity of Ap and Bnt horizons of a Duagh SiL	60
Figure 3. Effects of several N fertilizers on extractable Al of Ap and Bnt horizons of a Duagh SiL.	61
Figure 4. Effects of several N fertilizers on extractable Mn of Ap and Bnt horizons of a Duagh SiL.	62
Figure 5. Effects of several N fertilizers on extractable K of Ap and Bnt horizons of a Duagh SiL.	63
Figure 6. Effects of several N fertilizers on extractable Na of Ap and Bnt horizons of a Duagh SiL.	64
Figure 7. Effects of several N fertilizers on extractable Ca of Ap and Bnt horizons of a Duagh SiL.	65
Figure 8. Effects of several N fertilizers on extractable Mg of Ap and Bnt horizons of a Duagh SiL.	66

LIST OF PHOTOGRAPHIC PLATES

	<u>Page</u>
Plate 1. The effect of greenhouse applications of $\text{Ca}(\text{NO}_3)_2$ and $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ on production of barley grown on the Ap horizon of a Duagh SiL Check soil and the Ap of a Duagh SiL that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field.	90
Plate 2. The effect of greenhouse applications of CaCO_3 and CaSO_4 on production of barley grown on the Ap horizon of a Duagh SiL Check soil and the Ap of a Duagh SiL that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field.	90
Plate 3. The effect of greenhouse applications of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ on production of barley grown on the Ap horizon of a Duagh SiL Check soil and the Ap of a Duagh SiL that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field	91
Plate 4. The effect of greenhouse applications of $\text{Ca}(\text{NO}_3)_2$ and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ on production of barley grown on the Ap horizon of a Duagh SiL Check soil and the Ap of a Duagh SiL that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field.	91

INTRODUCTION

Solonetzic soils are very common in western Canada. In Alberta alone, the Solonetzic Order accounts for approximately 4.86 million hectares or nearly 30 percent of the arable land area mapped to date (Peters, 1973). The taxonomic designation Solonetzic defines an entire Order of soils and therefore includes those having a wide range of physical and chemical properties as well as productivity potentials. Overall, however, it is understood that Solonetzic soils show a reduction in yield of field crops and forages when compared to production potential afforded by soils of other Orders in immediately adjacent areas.

Numerous and complex physical-chemical interrelationships exist in all soil systems; however, the delicate balance of these equilibria are magnified in those of the Solonetzic Order. Analysis and probing of these systems as they exist in the field and are examined in the laboratory is essential in developing practices necessary for the amelioration of Solonetzic soils in the field.

In 1973, a study was undertaken to investigate:

- (a) the chemical properties of a Solonetzic soil having received moderate levels of nitrogen (N) in the form of various commercial fertilizers on an annual basis over a period of several years;
- (b) the chemical properties of a Solonetzic soil which received a heavy application of N in the form of NH_4NO_3 on an annual basis for an extended period; and
- (c) production of barley (Hordeum vulgare L.) grown in the Ap horizon of the same Solonetzic field soil receiving a moderate supply

of N in the form $(\text{NH}_4)_2\text{SO}_4$ for an extended period vs. production from an Ap horizon of the same soil receiving no N treatment in the field.

LITERATURE REVIEW

Characteristics of Solonetzic Soils

Naturally occurring soils of the Solonetzic Order have appreciable levels of Na in the A and B horizons of the soil profile. The taxonomic criterium of the Solonetzic Order dictates that accumulation of Na in the B horizon must be of sufficient magnitude so as to result in an exchangeable Ca to Na ratio value of 10 or less. Deflocculation of colloidal material is resultant under the influence of Na and downward movement of the dispersed material results in an accumulation in the area immediately beneath the A horizon (Peters, 1973). The B horizon of the Solonetzic soil, enriched with Na and clay, is designated Bnt. Organic staining of peds in this region is usually discernible, but the most significant feature is the extremely hard, impermeable (or nearly so) Bnt formed under the influence of accumulated Na affected clay. The resultant poor physical structure is the major cause of problems encountered in Solonetzic soils (Cairns and van Schaik, 1968; van Schaik and Pawluk, 1973).

Other problems have been identified in Solonetzic soils, and have been studied by many researchers. Nutrient deficiency (Cairns et al., 1962), Na toxicity (Skogley and Haider, 1969), denitrification (Myers of McGarity, 1972) and imbalance of Ca:Mg ratios (Halstead et al., 1958) are examples of problem parameters isolated. Many of the individual malaises listed may be due to undesirable levels of Na and low Ca:Na ratios of the B horizon found in these soils. In any case, the chemical properties of Solonetzic soils are known to precipitate

the poor structural characteristics, and it is generally thought that in order to ameliorate these soils, it is imperative to improve the infiltration rate of water into the profile (van Schaik and Cairns, 1969; Sandoval and Reichman, 1971). Virtually all soils in western Canada that have become Na affected (Solonetzic) and that have not been recently recharged by water with a high sodium absorption ratio (SAR) show some degree of leaching in the A horizon. This is accompanied by removal of basic cations and a corresponding increase in acidity of the upper horizons (Peters, 1973). In general, as a soil undergoes solodization a degree of desalinization occurs with time, although the impermeable columnar structure can remain resistant to any significant degradation. Salts that are mobilized eventually move into the C horizon, increasing the quantity of salts already present there.

Under good drainage conditions, soil sequences can range through the spectrum of solodization. In the field, Solonetz, Solodized Solonetz and Solod soils can be found in close proximity to one another (Cairns, 1961).

Cations in Soil Systems

The balance of exchangeable cations. Perhaps one of the most fundamental principles underlying the characteristics of soil systems is that all cations exist in a grand dynamic equilibrium. Much more is involved than a one dimensional relationship among activities of commingling cations. Complex equilibria exist among

specific cations within various phases of the soil system and interactions among these are intrinsic to soils. Cations are considered as:

- (a) soluble; dissociated in the soil solution. These are readily available for plant uptake.
- (b) exchangeable; associated with negatively charged sites on the clay and organic colloids. Exchangeable cations are also readily available to plants.
- (c) nonexchangeable; not associated with the exchange complex or with the soil solution. These cations may be part of primary and secondary soil minerals; organic complexes; or insoluble compounds when associated with particular anions.

Soluble, exchangeable and nonexchangeable soil cations are continually in a dynamic equilibrium and can shift from one phase to another in response to changing conditions in the soil (Doll and Lucas, 1973). Exchangeable cations affect many properties of soils and can directly influence potential productivity. The importance of the exchangeable Ca to Na ratio in Solonetzic soils is a most explicit example. The major exchangeable cations found in most mineral soils include Ca^{2+} , K^{+} , Mg^{2+} , NH_4^{+} , H^{+} , Al^{3+} , and Na^{+} . Smaller amounts of Mn^{2+} , Zn^{2+} , Cu^{2+} , and Fe^{2+} can also be present (Doll and Lucas, 1973).

Soil Ca. Ca is usually present as an exchangeable cation and can meet the nutritional requirements of plants solely by mass flow (Barber et al., 1962). Nonexchangeable forms may be found in primary minerals such as Ca-feldspars, calcite, dolomite and amphiboles. Ca

may also be present in the form of relatively insoluble salts such as CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the Csk horizons of Solonetzic soils (Cairns, 1972; Ryzhova and Gorbunov, 1975).

Soil Na. Dependant on location, groundwater may contain appreciable amounts of dissolved Na salts, particularly $(\text{Na})_2\text{SO}_4$ and NaCl . This water with a high SAR can move upwards with a rising water table into the soil profile and substantially raise the exchangeable sodium percentage (ESP) of the upper horizons. A deleteriously low exchangeable Ca:Na ratio may develop, complete with all the ramifications of deflocculation of soil colloids and poor physical structure. The movement of sodic water upwards into the soil profile is regarded as a major factor in the formation of Solonetzic soils (Pawluk, 1973). Subsequent rises in the groundwater can periodically recharge surface soil horizons with Na. Surface water with a high SAR also has potential to increase exchangeable Na in soils.

Soil K. Usually plant utilization of K is greater than that for other elements with the exception of N (Doll and Lucas, 1973). Sources of nonexchangeable K are primary minerals such as K-feldspars, muscovite and biotite micas. Gradual weathering can release substantial quantities of K, thus making it available. Secondary clay minerals such as illite, vermiculite and chlorite are also rich in K and these can act as reservoirs of this cation.

Fixation of exchangeable and soluble K is common with certain clay minerals, particularly vermiculite. Fixation is variable

by illite and only slight in the presence of montmorillinite (Doll and Lucas, 1973).

Soil Mg. Some soils have reserves of Mg present in primary materials such as biotite, serpentine, olivine and hornblende. Secondary clay minerals such as chlorite, vermiculite, illite and montmorillinite can also supply Mg. As in the case of K, release of Mg from clay minerals can be rapid (Doll and Lucas, 1973).

Soil NH_4 . This is a non-metallic ion which can be rapidly oxidized by soil microorganisms, or remain unchanged and become involved in inorganic reactions as a cation (Hausenbuiller, 1972). The effective diameter and coordination numbers of NH_4 closely resemble that of K, and both these species fit snugly into hexagonal pores on clay mineral surfaces (van Schaik and Cairns, 1974). NH_4 and K can undergo fixation by the same clay minerals and will readily substitute for one another in this regard (Lutz, 1966). NH_4 is a common constituent of soluble N fertilizers (Harre et al., 1971).

Soil H. Several causes of increased exchangeable H can be cited, including the activity of soil microorganisms (Hausenbuiller, 1972), inorganic hydrolysis reactions (Schofield and Taylor, 1954; McLean, 1973) and lattice decomposition of certain clay minerals (Coleman and Craig, 1961). The activity of H in solution is recorded in units of pH and an optimum level for many reactions is pH 6.5 to 7.0. Reactions involving soil microorganisms are particularly affected, including nitrification, mineralization and fixation of N (Alexander,

1967). Soil pH can also alter the availability of cations (Woodruff, 1967; Evans and Kamprath 1970) and required nutrients (Alexander, 1967; McLean, 1970; White et al., 1976).

Soil Al. Substantial documentation indicates that strongly acid soils often contain levels of Al toxic to plants (Magistad, 1925; Rigon and Pierre, 1932; Vlamis, 1953). Al is a major constituent of many mineral soils and can be released in substantial quantities by weathering (Evans and Kamprath, 1970; Coleman and Craig, 1961). When soil pH is near neutrality, Al is largely associated with OH ions, forming insoluble complexes that are unavailable to plants. However, under acidic conditions, Al can become readily available as exchangeable and soluble species (Llorca and Cruz-Romero, 1977).

Soil Mn. This element is required as a micronutrient by many plants (Alexander, 1967; McLean, 1970). References of Mn toxicity are numerous (Funchness, 1918; Pearson and Adams, 1967; McLean, 1970), particularly in acid soils. In soil systems, Mn is closely associated with the organic fraction and can be tenaciously chelated in organic and inorganic complexes (Viets and Lindsay, 1973; Lindsay, 1974). The oxidation state of Mn is very sensitive to redox potentials within the soil system.

Amelioration of Solonetzic Soils; Adjusting the Ca:Na Ratio

Effects of Ca salts. Ca salts, upon dissolution in the soil solution release Ca^{2+} , result in a net increase of exchangeable

Ca. Stabilization of colloids and subsequent improvement of structure is a direct result of increasing exchangeable Ca in Solonetzic soils (Ryzhova and Gorbunov, 1975).

Exchangeable Ca is much more vigorously adsorbed than is exchangeable Na. Rates of adsorption for Ca two to ten times greater than those of Na have been recorded when both these ion species are present in soil systems at equal concentrations (Ryzhova and Gorbunov, 1975). The Electric Double Layer Theory has proven useful in predicting the charge fraction of monovalent to total exchangeable cations. The relationships are reproducible for situations in which colloidal clay is employed exclusively as a cation exchanger (Bolt, 1955) and also in more complicated soil exchange systems (Pratt and Grover, 1964). Simply stated, this theory defines the charge fraction of monovalent cations vs. total cations in the diffuse double layer as a function of the concentrations (ionic activities) of monovalent and divalent cations in the equilibrium solution as well as the surface charge density of the exchanger involved. Simulation studies based on predictions from three distinct models: the Electric Double Layer Theory; a thermodynamic theory; and an empirical method proved that all three approaches were effective in describing Ca:Na exchange equilibrium (Poonia and Talibudeen, 1977). The models universally demonstrated that soils equilibrated with Ca and Na show a definite preference for adsorbing Ca. In addition, the standard free energy of exchange, a measure of ion selectivity, increases as the surface charge density of the exchange complex becomes greater. Increases in soil organic

matter or percent clay content of a soil leads to a greater tendency to preferentially adsorb Ca vs. Na. The accuracy of each of the mathematical models was verified with laboratory tests performed on a wide range of soils. The soils sampled represented significant differences in clay and organic matter content, cation exchange capacity (CEC), surface area, surface charge density, degree of salinity and reaction. Values for pH ranged from 5.9 to 9.9. In all cases, theoretical and laboratory results in defining Ca:Na exchange were extremely well correlated. Other studies in Ca:Na equilibrium corroborate the affinity of soil colloids to adsorb Ca over Na in soil solutions of relatively low ionic concentrations. However, substantial increases in electrolyte concentration do shift the adsorption equilibrium in a direction towards preference for retention of monovalent cations. This follows from the dilution law and valency effect (Moss, 1963; Clark and Turner, 1965). In equation form, the relationship is expressed as:

$$C = \frac{[M] \times f[M]}{\sqrt{[D]} \times f[D]} \quad \text{or} \quad C = \frac{Ma}{\sqrt{Da}}$$

Stated in a different form:

$$C = pMa - 1/2 pDa$$

where C = a constant representing an activity ratio for adsorption.

$[M]$ = molar concentration of monovalent cations.

$[D]$ = molar concentration of divalent cations.

f = activity coefficient.

a = activity of ion species.

Therefore, as concentrations (ion activities) for both monovalent and divalent species are simultaneously altered, the effective influence of divalent cations in the system is equal to the square root of the concentration (activity) of the divalent species, or one-half of the log of the activity of the species to base ten. As volume of diluent is decreased, and ionic strength of electrolyte raised, the increment in monovalent cation activity increases more rapidly than does the activity of divalent cations, such as Ca.

Once Na is desorbed from the exchange complex, there is real potential to move it deeper into the soil profile. Most Na salts are relatively soluble and this facilitates mobility. Downward movement of Na in the order four times as great as for Ca has been recorded in the upper horizons of a Duagh SiL (van Schaik and Cairns, 1969).

Naturally occurring Ca salts in the form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 are generally found in the C horizons of Solonetzic soils in western Canada (Cairns, 1972). These salts can be brought to the soil surface and mixed with upper horizons by deep plowing (Cairns, 1962; Antipov-Karataev, 1965) or added to the soil surface as an amendment and mixed with the upper horizons. However, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has given only erratic performance in supplying sufficient calcium concentrations to consistently improve physical properties of Solonetzic soils (Graveland and Toogood, 1963; van Schaik, 1967). Under field conditions, CaCO_3 also remains relatively insoluble. Increasing the solubility of Ca salts added to the upper horizons of Solonetzic soils has potential in affecting amelioration.

A biological vector in amelioration of Solonetzic soils.

Deeply rooted perennial vegetation such as established grass stands can preferentially accumulate Ca, Mg and K in aerial vegetative portions. This, then, can serve as a factor in selectively cycling Ca and other beneficial cations to the soil surface where they can contribute to continued solodization of a Solonetzic soil (Griffith and Walters, 1966; White, 1971). Although the total quantities of cations involved in this way may be limited under field conditions, the efficacy of vegetative cover as an ameliorative agent should not be underestimated. In addition to selectively cycling beneficial cations, plant roots have a direct effect in decreasing the bulk densities of subsoils. The potential for improvement in chemical and physical properties coupled with a reduction of surface evaporation resulting from the shading effects of foliage can effectively increase the leaching rate of displaced Na in the soil solution (Cairns and van Schaik, 1969).

Effects of salts that do not supply Ca. Salts other than

those that have Ca as the cationic species have proven efficacious in increasing the electrolyte concentration of the soil solution and ultimately improving the hydraulic conductivity or permeability of sodic soil profiles (Reeve and Tamaddon, 1965; van Schaik and Cairns, 1969). Of particular interest was the observation that in the course of working with the A and B horizons of a Duagh SiL; additions of salts of Ba, Mg, Ca, NH_4 and K significantly increased the hydraulic conductivity of this soil. However, the improvement in permeability

was reversed and the soil rapidly resealed when the electrolyte concentrations were subsequently decreased without allowing divalent cations to replace significant volumes of Na on the exchange complex (van Schaik and Cairns, 1969). This again underlines the importance of optimizing the ratio of exchangeable Ca to Na when considering amelioration of Solonetzic soils.

Van Schaik and Cairns (1969) also observed that the degree of permeability was related to the particular cation supplied by the salt; certain cations being more efficacious than others. Differing anionic species also influenced the beneficial effectiveness realized from increasing electrolyte concentrations of soil solutions. In the case of Duagh SiL, Ba was more effective in improvement of infiltration than were either Ca or Mg (van Schaik and Cairns, 1969). $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 appeared to have as much value for increasing infiltration rates of the A and B horizons of a Duagh SiL as did MgSO_4 and $\text{Mg}(\text{NO}_3)_2$, respectively. This implies that in this capacity, NH_4 has performance characteristics approximately equivalent to Mg.

There appears to be some potential in ameliorative methods for Solonetzic soils which involve the additions of salts to Na affected profiles. Any benefits gained would be a direct result of improved water infiltration into the soil profile. In choosing potential salts, several criteria are necessary. Cost performance and practicability of application are definitely important parameters. This consideration would surely rule out the use of Ba salts. Compounds supplying Ca and Mg usually are available at a lower cost and are usually present in the C horizon of Solonetzic soils.

However, the cost of bringing these to the soil surface can be prohibitive, especially when considering the potential for poor cost performance due to low solubilities of these compounds under field conditions, as discussed previously. NH_4 salts or compounds that readily form NH_4 in the soil environment have definite potential in this area. Salts such as $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and NH_2CONH_2 are widely used as fertilizers in western Canada and throughout the world (Harre et al., 1971). These are relatively inexpensive, highly soluble materials that supply NH_4 .

Solubility of Ca as affected by the addition of soluble salts in aqueous solutions. Tanjii and Doneen (1966) demonstrated that the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in aqueous solutions can be significantly increased by the addition of foreign ions. The presence of the added ions alters the ionic activities resulting in an increase in the dissociation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The solubility potential for a salt is expressed as a dissociation constant, and for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is expressed as:

$$K_{(\text{CaSO}_4)} = \frac{A_{\text{Ca}} \times A_{\text{SO}_4}}{A_{(\text{CaSO}_4)}}$$

where $K_{(\text{CaSO}_4)}$ = the dissociation constant for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

A_{Ca} , A_{SO_4} , $A_{(\text{CaSO}_4)}$ = ionic activities of Ca, SO_4 , and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, respectively. $A_{(\text{CaSO}_4)}$ is equal to unity in aqueous solutions.

Therefore: $K_{(\text{CaSO}_4)} = A_{\text{Ca}} \times A_{\text{SO}_4}$

Cations other than Ca introduced into this system can become associated with SO_4 and thus reduce the activity of SO_4 (A_{SO_4}). A corresponding increase in the activity of Ca occurs as the system equilibrates to maintain the dissolution constant, $K_{(\text{CaSO}_4)}$, and this yields a net increase in the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Tanjii, 1969). The solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is also greatly enhanced if the foreign electrolyte contains certain anions (eg., Cl or NO_3). These anions compete with SO_4 for association with Ca and thereby increase the dissociation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ resulting in a net increase in the concentration of Ca in solution (Tanjii and Doneen, 1966).

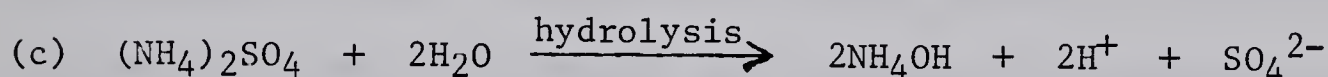
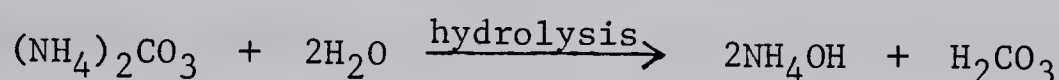
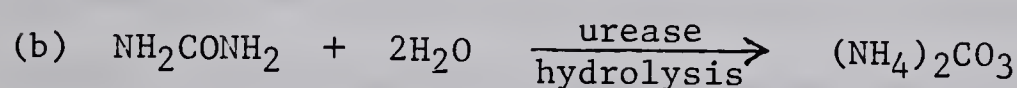
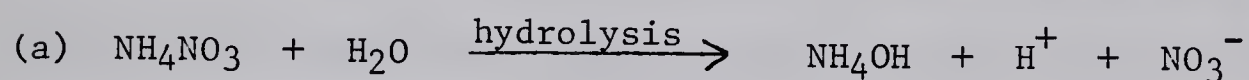
Applications of N Fertilizers

Formulations of N fertilizers. The single nutrient required in greatest quantity by most major agronomic crops is N. Particularly under sustained, intensive agronomic production, there is a need to regularly supplement this element in larger quantities than other nutrients for crops which are incapable of fixing atmospheric N. There is no doubt that the use of N fertilizers has escalated rapidly in the recent past, not only on lands that previously went unfertilized but also as increasingly higher rates have been added to soils that have had regular applications of N.

There appears to be a definite shift towards preference of high analysis gaseous formulations of N fertilizers and to various liquid solutions of N; probably mainly in deference to expediency in handling and application. Nevertheless, soluble N salts are still

widely used as fertilizers (Harre et al., 1971).

Several common N fertilizers. Additions of NH_4 salts or those that rapidly form NH_4 after initial reaction in the soil yield an abundance of NH_4 ions. Hydrolysis is a common step in the dissociation of soluble N salts in soils as illustrated in the following reactions:



Under field conditions, additions of the salts described will largely result in a net accumulation of NH_4OH . This relatively weak base will dissociate in soil solutions into component NH_4 and OH ions. A direct effect of additions of NH_4NO_3 , NH_2CONH_2 and $(\text{NH}_4)_2\text{SO}_4$ then, is to increase the abundance of soil NH_4 .

The Potential for N Fertilizers as Ameliorants of Solonetzic Soils

Biological effects of N fertilizers. The majority of N added to soils is usually assimilated by plants in the forms NH_4 and NO_3 (Tisdale and Nelson, 1967). Lesser amounts of NH_2CONH_2 may also be absorbed in molecular form. In the capacity of supplying a nutrient essential for plant growth, N fertilizers can dramatically increase

root activity and dry matter yield of crops. Cairns et al. (1967) found that on a Duagh SiL, annual applications of NH_4NO_3 (150 and 300 kg/ha N) over a period of five years significantly increased the mean dry matter yield of brome grass to 4,794 and 6,779 kg/ha, respectively, as compared to a yield of 1,506 kg/ha for an unfertilized check. Root activity and development were also stimulated by applications of N fertilizer. Improved root penetration and reduction of soil bulk density aids infiltration of water into the soil profile, increasing the potential for leaching of Na (Cairns et al., 1967). As well, substantial increases in vegetative growth provide potential for additional amounts of organic matter (OM) to become incorporated into Solonetzic soils. Increased OM content directly contributes to a reduction in soil bulk density and promotes soil flocculation which improves the physical structure of soils (USDA, 1954). The selective cycling of beneficial cations such as Ca, Mg and K by vegetation established on Solonetzic soils and their contribution to solodization of these soils is documented (Griffith and Walters, 1966; George, 1967; White, 1971). Additions of N fertilizers stimulate plant growth and root production, potentially increasing the total quantities of cations cycled in this manner.

The effect of added NH_4 on exchange equilibria. Additions of soluble salts raise the activity of free electrolyte in the soil solution and can improve flocculation of soil colloids, ultimately increasing the rate of water infiltration into Na-affected soils (Reeve and Tamaddon, 1965; van Schaik and Cairns, 1969). Van Schaik and Cairns (1969; 1974) also report that NH_4 added to the A and B

horizons of a Duagh SiL as well as to bentonite suspensions markedly improved flocculation of soil colloids with subsequent increases in the rate of hydraulic conductivity. However, dilution of the system and the resultant reduction in the concentration of electrolyte initiated a rapid resealing of Solonetzic soils if divalent cations had not replaced Na on the exchange complex. NH_4 appeared to be about as effective as Mg in improving water infiltration into a Duagh SiL, although both cations were less efficacious than Ca in this respect (van Schaik and Cairns, 1969). Working with Na-affected soils, Pinskiy (1973) showed less stability of bonds between soil colloids and NH_4 vs. the bonding energies observed for exchangeable Ca. This suggests Ca saturated soil systems are preferred over those saturated with NH_4 . Van Schaik and Cairns (1974) reported that Ca-montmorillinite tactoids were approximately twice the size of corresponding NH_4 tactoids, thereby inducing a better state of flocculation of soil colloids, and resultant improvements in hydraulic conductivity were greater with Ca additions.

NH_4 added to soils is expected to replace exchangeable Na at a greater rate than exchangeable Ca, as the energy of adsorption for Na is less than for Ca (Ryzhova and Gorbunov, 1975; Poonia and Talibudeen, 1977). Once Na has become desorbed from the exchange complex, the high solubility of common Na salts in soil solution leads to a potentially high downward mobility for Na. Van Schaik and Cairns (1969) have reported that rates of leaching of Na may be four times greater than for Ca in the A and B horizons of a Duagh SiL. Addition of NH_4 , then, has potential to increase the Ca:Na ratio of

Solonetzic soils. Also, nitrification of NH_4 generates H ions which can occupy exchange sites on soil colloids and desorb Na from these sites.

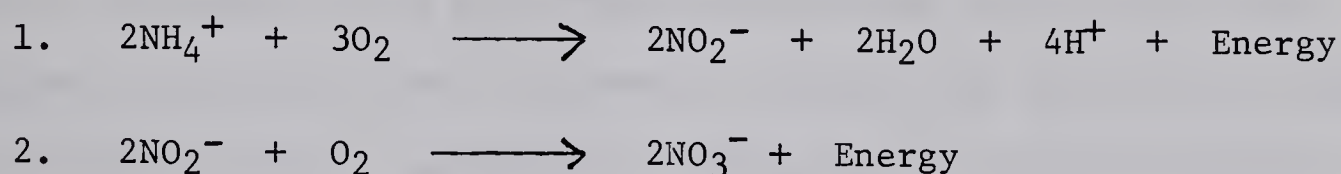
The effect of added NH_4 on the solubility of Ca salts. The ability of additions of foreign ions to improve the dissociation of relatively insoluble salts has been demonstrated in the case of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Tanji and Doneen, 1966; Tanji, 1969). Salts of NH_4 or those that rapidly form this species in soil solution supply NH_4 ions which become associated with SO_4 ions and theoretically increase the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This has significant importance in situations in which $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ has been supplied as an amendment in an effort to ameliorate Solonetzic soils. Also, foreign anions supplied with N fertilizers can substantially contribute to increasing the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. For example, NH_4NO_3 supplies NO_3 that, upon association with Ca provided by $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, forms a very soluble compound, and thereby substantially increases the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Carter et al. (1977) reported that additions of NH_4NO_3 increased the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in distilled water by 30 to 40 percent. In the field, repeated yearly applications of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ plus NH_4NO_3 to a Brown Solodized Solonetz for a period of four years significantly increased exchangeable Ca over applications of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ alone. This clearly indicates that NH_4NO_3 can, in fact, increase the solubility of this Ca salt under field conditions (Carter et al., 1977). NO_3 may be applied as an anionic species of N fertilizer or may be generated as NH_4 undergoes nitrification.

Nitrification also yields an abundance of H ions which can play an important role in the solubilizing of CaCO_3 added to the surface horizons of Solonetzic soils. H can become associated with the anionic component of CaCO_3 , yielding HCO_3^- and H_2CO_3 . This reaction liberates Ca which can be adsorbed by soil colloids (Antipov-Karataev, 1954).

The Effects of Repeated N Fertilizer Treatments

The acidification potential for N fertilizers. Repeated applications of common N fertilizers have a potential to acidify soils (Adams and Pearson, 1968; Bolton et al., 1970). McCoy and Webster (1977) have reported that additions of N at rates as low as 11 kg/ha per year over a period of 40 years significantly reduced pH and adversely affected the production of alfalfa on a Luvisolic soil. Pierre (1928; 1933) described a simple mathematical model to predict the potential effects that added fertilizer compounds have on soil reaction. The model suggested that the combined total of the equivalents of Ca^{2+} , Mg^{2+} , K^+ and Na^+ supplied, subtracted from the equivalents of SO_4^{2-} , Cl^- , H_2PO_4^- and $\text{N}/2$ would indicate the potential acidity or basicity of the added fertilizer. Positive values were interpreted as a measure of acidity, negative values denoted basicity. The concept is not completely definitive, however, because it does not differentiate between the form of N added, whether it is NH_4 or NO_3 , nor the fact that although certain salts such as KCl are neutral in aqueous solution, they can increase the activity of H ions in soil systems.

The transformation of NH_4 to NO_3 : nitrification. Additions of NH_4NO_3 , NH_2CONH_2 and $(\text{NH}_4)_2\text{SO}_4$ to soils net an initial increase of NH_4 in the soil (Hausenbuiller, 1972). NH_4 may remain unaltered as a cation and form part of the nonexchangeable, exchangeable and soluble phases of soil systems (Hausenbuiller, 1972; van Schaik and Cairns, 1974). However, under conditions favorable for nitrification, soil NH_4 is oxidized to NO_3 by autotrophic soil microorganisms in the following stepwise reactions:



The major organisms involved in nitrification are Nitrosomonas species in step 1 and Nitrobacter species in the subsequent stage, although other soil microorganisms are thought to make minor contributions (Tisdale and Nelson, 1966). Under most soil conditions, the second reaction proceeds at a slightly more rapid rate than the first and a net accumulation of NO_3 results (Tisdale and Nelson, 1966; Hausenbuiller, 1972). The rate of nitrification is dependant on concentrations of NH_4 and NO_3 , pH, populations of nitrifying organisms, the degree of aeration (O_2 supply), moisture and temperature of the soil environment (Tisdale and Nelson, 1966; Alexander, 1967). Cairns (1963) has indicated that nitrification of NH_2CONH_2 added to a Duagh SiL proceeded rapidly and that nitrification of applied N was relatively complete. Over a period of five years, applications of NH_2CONH_2 , NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ each at a rate of 112 kg/ha N per year resulted

in net decreases of pH within the Ap horizon of a Duagh Ap to 5.2, 4.8 and 4.0, respectively, as compared to a pH of 5.3 for an unfertilized Check (Cairns, 1968).

The potential for N fertilizers to acidify soils is dependant on several factors. An important consideration is the amount of N supplied in the form of NH_4 . It is expected that $(\text{NH}_4)_2\text{SO}_4$ would decrease soil pH to a greater degree than additions of NH_4NO_3 when both supply equivalent amounts of N (Hausenbuiller, 1972). One-half of the N of NH_4NO_3 is supplied as NO_3 and is not subject to nitrification. In order to furnish the same rate of N as the NH_4NO_3 treatment, additions of $(\text{NH}_4)_2\text{SO}_4$ will supply twice the concentration of NH_4 and thereby have the potential to generate twice as many H ions during nitrification.

Hydrolysis products of N fertilizers. As well as regulating the portion of N supplied as NH_4 , the structure of a particular N fertilizer determines the products formed when these N fertilizers are added to soils. The hydrolysis products of N fertilizers can markedly influence soil reaction. Upon dissociation in soil solution, NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ yield an abundance of NH_4 . Hydrolysis is resultant, as energy potentials favor the formation of NH_4OH and cause cleavage of H_2O molecules, with a concomitant release of free H ions into the soil solution. In the case of NH_2CONH_2 , however, $(\text{NH}_4)_2\text{CO}_3$ is initially formed under the influence of urease (Hausenbuiller, 1972). $(\text{NH}_4)_2\text{CO}_3$ in turn hydrolyzes to NH_4OH and H_2CO_3 ; the latter a weak acid. Therefore, the activity of H generated

by hydrolysis is effectively reduced by CO_3 ; and OH which dissociates from NH_4OH can become available to neutralize other acidic species in the soil which were not a direct product of the hydrolysis of NH_2CONH_2 . Therefore, the initial hydrolysis reactions usually result in a net increase in soil pH soon after the addition of NH_2CONH_2 . However, subsequent nitrification of the NH_4 supplied by NH_2CONH_2 will ultimately depress soil pH, although overall the actual degree of depression is less than for additions of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$.

Cations dissociated from salts, including NH_4 compounds, can displace H as well as Al and Fe from soil colloids (Chen, 1965); and Al and Fe can undergo hydrolysis to form free H (Coleman and Thomas, 1967; McLean, 1973). When the accompanying anions to NH_4 are NO_3 and SO_4 , these cannot effectively reduce the activity of H , whether it is a result of desorption or a product of hydrolysis and consequently soil pH decreases. On the other hand, anions such as CO_3 and HCO_3 are very effective in neutralizing H in soil solution (McCoy, 1973). Therefore, the companion ion, or those formed upon reactions within the soil are important to consider when dealing with the acidic nature of N fertilizers added to soils.

Other salts that may contribute to soil acidification.

Additions of soluble salts other than NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ can cause net increases in soil acidity. Many compounds that are neutral in aqueous solution in fact have acidic reactions in soil systems -- eg. KCl and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. These supply cationic species which can desorb H from soil colloids and directly contribute to a lower pH; as well

as cause desorption of Fe and Al which subsequently undergo hydrolysis and release H into soil solution. The presence of Cl or SO_4 has no effect in reducing the activity of free H in the soil solution and pH falls. In addition, Cl and SO_4 ions are taken up in much lower quantities than the added cations K or Ca (or for that matter NH_4). This leaves a large proportion of the added anions remaining in solution and these can selectively leach bases within the soil profile. In particular, Cl and NO_3 form soluble salts with Ca (Tanji, 1969) and additions of these anions can enhance the loss of Ca from the upper horizons of a soil profile.

The Effects of Soil Acidification

Potential losses due to acidification. Data presented by Crowther (1936) demonstrated that applications of $(\text{NH}_4)_2\text{SO}_4$ markedly depressed soil pH and leached exchangeable Ca to the point that after 20 years of N fertilizer application, liming was required in order to optimize yields. Earlier, Voelcker (1874) reported that greatly increased concentrations of Ca and Mg were found in drainage waters collected from fields receiving NH_4 salts over a period of four years. More recently other authors have indicated significant decreases in soil pH and corresponding loss of productivity from applications of N fertilizers, particularly those made over a long period of time (Adams et al., 1967; Bolton et al., 1970; McCoy and Webster, 1977).

Applications of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ at rates to supply 112 kg/ha N per year significantly depressed pH, with the $(\text{NH}_4)_2\text{SO}_4$

being the more severe treatment (Cairns, 1968). The application of NH_2CONH_2 to supply the same level of N only reduced pH to 5.2 as compared to 5.3 for an unfertilized Check. However, all three fertilizers markedly increased brome grass yields over a five year period. Cairns et al. (1967) also reported that applications of 150 and 300 kg/ha N per annum of NH_4NO_3 over a five year period significantly increased brome grass production. The NH_4NO_3 treatments decreased levels of exchangeable Na and K and caused an increase in the exchangeable Ca:Na ratio. The same trends were noted for Halkirk loam and Torlea loam, both Dark Brown Solonchets. Yield of brome grass was increased by applications of 449 kg/ha N as treatments of NH_4NO_3 and NH_4NO_3 plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ on Hemaruka silty clay loam over a period of four years (Carter et al., 1977). The latter treatment slightly increased the yield of brome grass, but at the same time significantly depressed the pH of both the Ap and Bnt horizons as compared to NH_4NO_3 alone. The potential for N fertilizers to increase yields is well established, but certain N sources markedly depress soil pH and increase the leaching of desirable cations.

Al toxicity. Toxicity due to the presence of available Al is generally regarded as a major cause of malaise on acid soils (Vlams, 1953; Pearson and Adams, 1967; Hoyt, 1977). As discussed earlier, Al is a major constituent in most mineral soils and as such can be released in appreciable quantities by chemical weathering (Evans and Kamprath, 1970; Coleman and Craig, 1961). Al thus released can become tenaciously adsorbed to soil colloids, although it can be

desorbed by other soil cations, including H (Chen, 1965; Llorca and Cruz-Romero, 1977) and NH_4 (Chen, 1965; Cabrera and Talibudeen, 1977). This desorption can be particularly rapid if there is a net increase of cations, as results with additions of NH_4 ; and especially when H is generated from nitrification of NH_4 . At soil pH approximately 5.5 and less, trivalent Al exists in soil systems. At pH 5.5 and above, Al reacts with OH to yield Al-OH complexes. The particular Al-OH species formed is pH dependant and as pH rises, AlOH^{+2} , Al(OH)_2^+ and Al(OH)_3 are formed (Clark, 1965; Sivasubramiam and Talibudeen, 1972; Llorca and Cruz-Romero, 1977). Al-OH species are unavailable for plant uptake, but OH complexing is reversible and decreases as pH falls. Decreases of soil pH to 5.5 and below into the range of 5.0 and less cause complete dissociation of Al-OH complexes and trivalent Al becomes available (Sivasubramiam and Talibudeen, 1972).

Several researchers report that soil Al can restrict the elongation and development of plant roots in acidic soils (McLeod and Jackson, 1965; Adams and Lund, 1966; Evans and Kamprath, 1970). Others have indicated that Al may interfere with the upward translocation of P (Pierre and Stuart, 1933; Foy and Brown, 1963, 1964), as well as the availability of P to plants (White and Taylor, 1977). Hoyt and Nyborg (1971a) reported results from analysis of 40 acid soils and found that the yields of barley, rapeseed and alfalfa were highly correlated with extractable soil Al. As well, the yields of rapeseed and alfalfa were correlated with soil pH as was plant uptake with levels of extractable soil Al.

Mn toxicity. Poor growth on acid soils has also been attributed to toxic levels of Mn, although this is generally thought to be less important than Al toxicities in these soils (Pearson and Adams, 1967; Hoyt and Nyborg, 1972). Mn is required in small amounts as a micronutrient (Alexander, 1967; McLean, 1970) and exists in soils in the solution phase and in Mn complexes and chelates with the organic fraction (Viets and Lindsay, 1973). The organic fraction, in fact, can chelate a large percentage of soil Mn (Lindsay, 1974). This author also reports that the availability of Mn is highly dependant on H activity and low pH enhances Mn toxicity. As well, the form of Mn is highly correlated to the redox potentials within soil systems. Hoyt and Nyborg (1971b) also found that yields of barley, rapeseed and alfalfa were correlated with available Mn. As well, correlations were identified between plant uptake and levels of extractable soil Mn.

Other problems associated with soil acidity. It is generally thought that H ions do not directly cause toxicity symptoms in plants grown on acidic soils (McCoy, 1973). However, it is known that as well as governing the toxic levels of certain ions in the soil, the activity of H ions may alter the requirement for certain plant nutrients. It appears that the availability of Ca (Kamprath, 1970; Doll and Lucas, 1973), Mg (Adams and Pearson, 1967; Kamprath, 1970), P and Mo are affected by changes in soil pH (Kamprath, 1970). The question of deficiency of these nutrients is considered to be of minor importance, however, when assessing problems associated with acidic soils (McCoy, 1973).

N transformations as affected by soil acidity. The cycling of N within soils can be subject to alterations by changes in pH. The conversion of organic N to inorganic NH_4 proceeds most rapidly when soil pH is near neutrality (Alexander, 1967). Mineralization, however, continues at extremely low pH because a diverse group of microorganisms is involved, and the roles played by various members changes with pH. One of the controlling factors in the rate of nitrification is soil pH. The rate is drastically reduced as soil pH dips below 6.0. However, some nitrification proceeds below this level and it is thought that there is no exact limiting degree of acidity (Alexander, 1967). Activity of H also affects the nodulation of plants that have an ability to fix atmospheric N by depressing the activity of facultative symbiotic bacteria Rhizobia meliloti. Cairns (1972b) found that increasing the pH of a Duagh SiL increased the availability of N.

Methods of correcting acid soil malaise. The presence of organic residues has had some positive effects in improving production on acid soils (Adams and Lund, 1966; Evans and Kamprath, 1970). McLean (1970) reported that agronomic production on acidic peat and muck soils usually responded positively when soil pH was brought up to 5.2; but that further beneficial results were not generally noted by bringing soil pH above this level. One reason suggested for this observation is the fact that organic matter has a strong affinity for adsorbing and complexing ions, thereby suppressing the toxic effects of these in acidic soils. This effect has been reported for Al in mineral soils as well (Sivasubramaniam and Talibudeen, 1972; Hoyt and Turner, 1975) and also for Mn (Viets and Lindsay, 1973).

Hoyt and Turner (1975) indicated that additions of alfalfa meal at levels equalling 1.5 and 3.07% of total soil weight decreased the exchangeable Al available to plants to less than one-half of the quantities available with no additions of organic residue. The realization that the quantities of organic residue required to be effective are huge and therefore prohibitively costly on a field scale, as well as the fact that the effects of reduced Al were temporary and measurable only to 24 weeks after application led the authors to conclude that high levels of organic matter were no substitute for proper liming practices on severely acidic soils.

Liming of soils provides for an abundance of anions which react with and reduce the activity of soil H. This is correlated with increases in the activity of basic species, particularly OH, which associate with toxic cations, including trivalent Al, and render these unavailable for plant uptake (Clark, 1965; McLean, 1970). It has been suggested that liming to neutrality is not necessary and that supplying basic ions to a point to limit the availability of toxic cations, particularly Al, to tolerable levels is sufficient (Kamprath, 1970). Hoyt (1977) shows agreement and suggests that, as a guide, liming to a pH of 5.5 should be adequate to prevent most problems encountered with production for most agronomic crops on acidic soils. The exception is alfalfa, for which a minimum pH of 6.0 is recommended. McLean (1970) also supports the concept that toxicities may be satisfactorily overcome by pH adjustments to levels below pH 7.0, but points out the availability of Ca, Mg, P, K and several other micronutrients, as well as microbial activity and N fixation, are

maximized near neutrality.

Summary of Literature Review

The potential role of some N fertilizers in amelioration of Solonetzic soils. The literature provides support for a concept that implies applications of N salts commonly used as fertilizers may have utility in amelioration of Solonetzic soils. There is evidence that NH_4NO_3 , NH_2CONH_2 , and $(\text{NH}_4)_2\text{SO}_4$ can contribute to improvements in the physical and chemical properties of Solonetzic soils through a variety of means including: biological cycling of desirable cations; stimulation of root production; improving the exchangeable Ca:Na ratio by influencing selective desorption of Na; and directly improving the flocculation of soil colloids. As well, added N fertilizers have potential to perform a key role in increasing the solubility of Ca salts added to Solonetzic soils as ameliorative agents.

At the same time, additions of NH_4NO_3 , NH_2CONH_2 , and $(\text{NH}_4)_2\text{SO}_4$ are known to ultimately increase the activity of soil H. The degree of depression of soil pH is dependant on several parameters, including the fertilizer material employed, the rates added and the period over which applications are made as well as other considerations such as the rate of nitrification and the buffering capacity of the soil in question. Soil acidity may contribute to a detrimental situation complete with toxic levels of cations such as Al and Mn, and management practices to raise the soil pH to a more desirable level may be required. Nitrification in a Duagh SiL is known to proceed rapidly and relatively completely, with a concomitant drop in pH.

The possibility of utilizing certain N fertilizers to ameliorate the poor qualities intrinsic to Solonetzic soils is worth consideration. At the same time, secondary effects of ameliorative treatments should be closely monitored. Optimizing the potential for agronomic productivity necessarily involves the concept that productivity is a function of many interrelated factors including the overall ability of the entire soil body to provide a desirable environment for the particular crop cultivated.

MATERIALS AND METHODS

Description of Field Soils Sampled

Soils studied were of a Duagh SiL series sampled from two individual trial sites located on the Canada Department of Agriculture Solonetzic Soil Substation near Vegreville, Alberta. These soils are representative of a Black Solonetz developed on saline lacustrine parent material (Cairns et al, 1969; Toogood and Cairns, 1973). The major clay minerals which constitute the clay fraction of the Duagh SiL series are montmorillinite (55 percent) and illite (20 percent) (Dudas and Pawluk, 1969).

One of the trials sampled was initiated as a randomized, replicated block under an established stand of brome grass (Bromus inermis). Commencing in 1963, and on an annual basis thereafter, spring applications of three individual fertilizer treatments were made for a total of ten years. Each supplied 112 kg/ha N per year. The N fertilizers, each of which constituted a separate treatment, were NH_4NO_3 , NH_2CONH_2 and $(\text{NH}_4)_2\text{SO}_4$. These, plus a check plot, receiving no N fertilizer were individually replicated three times. A detailed schematic and description of the "Various Forms of N Trial" appears in Appendix A. Total production of brome grass was recorded on a regular basis. Also, an effort was made to monitor the effects that each of the various forms of N, applied at a moderate rate, had on soil properties.

The other field trial involved repeated yearly applications of high rates of NH_4NO_3 for a period of 12 years. The annual rate of N supplied by the fertilizer treatment was 300 kg/ha vs. none for the

check area. The trial, initiated in 1961, was established in a stand of brome grass (Bromus inermis) and Kentucky bluegrass (Poa pratensis L.). A diagram of the "Fertility Test" is found in Appendix B.

Sampling of Field Soils for Laboratory Analysis

Soil samples were collected in May 1973, using a mechanical core sampler. The last applications of N fertilizers immediately preceding sampling were made in 1972. Three cores were taken from each replicate of individual treatments in the "Various Forms of N Trial." All cores were sectioned into 2.5 cm segments in the Ap horizon, and into 5.0 cm segments in the Bnt horizon. The depth of the Csk horizon was determined in the field, and a section 5.0 cm above this layer was retained; all material below this sample depth was discarded. The segmented core samples from specific depths were bulked for each treatment, and replicates kept separate.

Cores were also taken at appropriate depths from the "Fertility Test." These were taken in a paired sample format, which was conducive to the application of a t-test in statistical analysis of data. Again, the Ap and Bnt horizons were divided into 2.5 and 5.0 cm sections, respectively. In this case, the top 10 cm of the Csk horizon was retained as two separate 5.0 cm segments. Ten paired core samples, in a linear orientation approximately 1 m apart were taken throughout the length of the NH_4NO_3 treated and check areas.

Preparation of Soil Samples for Laboratory Analysis

Sectioned samples were dried in a forced air chamber at 70°C for 24 hours. Microstructure of each sample was then determined as was

color when the soil was both moist and dry. Samples were then ground and passed through a 2 mm sieve. Extraneous materials including small stones and undecomposed plant residues were discarded.

Field Soil Sampling and Preparation for Greenhouse Study

In the fall of 1973, bulk soil samples were taken from the Ap horizons (0-10 cm) of the $(\text{NH}_4)_2\text{SO}_4$ treatment and Check in the "Various Forms of N Trial" at Vegreville. Soils were collected from each of the replicates, and spread to air dry. These samples were then screened to remove stones and foreign debris, and thoroughly mixed. The samples were again screened to 10 mm and stored for greenhouse use. A subsample of each Ap horizon was also taken, ground to pass a 2 mm screen, and retained for analysis in the laboratory.

Laboratory Analysis: Soils

Extractable cations and cation exchange capacity. The method used for extracting cations from soil is described in the U.S. Department of Agriculture (USDA) Handbook No. 60 (1954). This procedure utilizes $1\text{N } \text{NH}_4\text{OAc}$ ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) and essentially was followed in detail. However, the extracting solution was adjusted to pH 6.5 vs 7.0 specified in Handbook No. 60. It is felt that NH_4OAc adjusted to pH 6.5 results in a more meaningful extraction of soils involved in this study (R. R. Cairns, personal communication). The slight alteration of pH was incorporated to parallel previous analyses conducted at the Solonetzic Soil Substation at Vegreville.

Determination of cation exchange capacity (CEC) was accomplished by the method described in Handbook No. 60 (1954). This involves

replacing all exchangeable cations with Na, and subsequent removal of this species from the exchange sites by repeated quantitative washings with NH_4OAc . A reading of concentration of Na in the final leachate gave an accurate measure of CEC.

Soluble cations: extraction. Soluble cations were extracted with deionized water in a 1:5 (soil:water) suspension. The method is outlined in USDA Handbook No. 60 (1954).

Soil reaction. Soil pH was measured in a soil:deionized water suspension (1:2.5) after equilibration. A glass electrode pH meter was employed in making readings.

Electrical conductivity. EC was determined in the 1:5 extract suspension using a single electrode conductivity bridge with expanded scale. Final measurements were expressed as mmhos/cm.

Quantitative determination of soil cations. Measurements of Na and K in soil extracts were made using a flame spectrophotometer. The determination of both these species was completed for extractable and soluble cations using standard curves established with appropriate extracting solutions. Final quantitative readings of Na in the determination of CEC were also measured by flame photometry.

Concentrations of extractable and soluble Ca, Mg, Mn and of extractable Al were measured by atomic absorption spectroscopy, following methods described by Isaac and Kerber (1971). The flame used was air-acetylene. A quenching solution of La_2O_3 to provide 1 percent (W/V) La in the final dilution was utilized in determination of Ca and Mg.

Exchange acidity. The exchange acidity of soil samples was determined using BaCl_2 -Triethanolamine as reported by Peech (1965).

Greenhouse Study

Soils utilized. Soils gathered from the Ap horizons of the $(\text{NH}_4)_2\text{SO}_4$ treated and Check areas of the "Various Forms of N Trial" at Vegreville were used as the basis for a greenhouse experiment. After preparation of the bulk samples, the moisture content of each soil was determined at 1/10 and 15 atmosphere using a pressure system and a pressure plate/membrane assembly, respectively. Oven dry weight was determined by drying in a forced air oven at 105°C for 24 hours.

Lime requirement to raise soil pH to 6.5 (1:2½, soil:water ratio) in each of the field soils was also determined.

Greenhouse treatments. Soils collected from the field were potted to a weight of 1,500 g (O.D. basis), and seven treatments for each field soil were initiated. These included a Control, as well as applications of $(\text{NH}_4)_2\text{SO}_4$, $\text{Ca}(\text{NO}_3)_2$, CaSO_4 (with and without $(\text{NH}_4)_2\text{SO}_4$), and CaCO_3 (with and without $(\text{NH}_4)_2\text{SO}_4$). A complete description of greenhouse treatments is found in Table 1. The Check Ap horizon from the field is designated A and $(\text{NH}_4)_2\text{SO}_4$ treated as B.

Finely ground quantities of CaSO_4 (treatments A4, A5, B4, B5) and CaCO_3 (treatments A6, A7, B6, B7) were thoroughly mixed with the Ap horizons, and these were replaced in appropriately labelled pots. CaSO_4 was added to supply 286 ppm Ca (O.D. basis), while CaCO_3 additions were made to alter the soil reaction of each particular field soil to a pH of 6.5 (1:2½). This required addition of 1,528 ppm of Ca to the

Table 1. Greenhouse treatments applied to the Ap horizon of a Duagh SiL that had received long-term repeated applications of $(\text{NH}_4)_2\text{SO}_4$ in the field and an Ap horizon of a Duagh SiL Check

Field Soil	Treatment No.	Greenhouse Treatments		
		Treatment	ppm (O.D. basis) +Total N Supplied	Total Ca Supplied
Check	A1	Control	0	0
	A2	$(\text{NH}_4)_2\text{SO}_4$	200	0
	A3	$\text{Ca}(\text{NO}_3)_2$	200	\dagger 286
	A4	CaSO_4	0	286
	A5	$\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$	200	286
	A6	CaCO_3	0	1,528
	A7	$\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$	200	1,528
$(\text{NH}_4)_2\text{SO}_4$	B1	Control	0	0
	B2	$(\text{NH}_4)_2\text{SO}_4$	200	0
	B3	$\text{Ca}(\text{NO}_3)_2$	200	\dagger 286
	B4	CaSO_4	0	286
	B5	$\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$	200	286
	B6	CaCO_3	0	5,733
	B7	$\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$	200	5,733

\dagger Treatments supplying N were applied in two stages. One-half of the total amount was applied at seeding; the balance being broadcast 5 days after barley plants emerged.

\ddagger Ca was supplied in two stages corresponding to N application. CaCO_3 treatments were added to give a final soil pH approximately equal to 6.5 (1:2½ soil:water).

Ap horizon of the Check (treatments A6, A7) and 5,733 ppm of Ca to the $(\text{NH}_4)_2\text{SO}_4$ treated field soil (treatments B6, B7).

The uppermost 8 cm of soil in each pot was then removed and set aside. An aqueous solution of KH_2PO_4 to supply 40 ppm P and 50 ppm K was uniformly distributed on the surface of the soil remaining in each pot. The soil previously set aside was then accurately replaced for both field soils for the following greenhouse treatments: Control (A1, B1); CaSO_4 alone (A4, B4); and CaCO_3 alone (A6, B6).

Nitrogen treatments, in aqueous solution, were also applied as required at this time. $(\text{NH}_4)_2\text{SO}_4$ was added by pipette to pots labelled $(\text{NH}_4)_2\text{SO}_4$ (A2, B2), $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ (A5, B5) and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ (A7, B7). $\text{Ca}(\text{NO}_3)_2$ treatment was also made to each of the Check and $(\text{NH}_4)_2\text{SO}_4$ treated field soils (A3, B3). Initial N treatments supplied 100 ppm N which was one-half of the total N applied in the greenhouse. This was done to prevent potential inhibitory effects that high concentrations of this element may have on germination of plants. The soils treated with N were then refilled with the volumes of each appropriate soil previously removed. All greenhouse treatments were replicated four times.

Barley (Hordeum vulgare L., cv. Galt) was then seeded into each pot at a depth of approximately 4 cm. Each pot was then watered to 1/10 atmosphere moisture content. When approximately 50 percent of the available moisture had been used, the soils were wetted gravimetrically to 1/10 atmosphere moisture content.

Applications of $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$ were made to all greenhouse treatments that had previously received these same additions,

five days after barley plants had emerged. N solutions were uniformly broadcast by pipette over the surface of the soil of each pot treated. Care was exercised to prevent contact of the solution with exposed vegetative portions of the barley shoots. This, then, brought total application of N to 200 ppm in the individual pots designated to receive these treatments. Ultimately, the amount of Ca supplied by the $\text{Ca}(\text{NO}_3)_2$ treatment was equal to 286 ppm.

Barley plants were eventually thinned to ten plants per pot and the experiment continued for a total of 45 days, at which time plants were well-tillered. A photoperiod of 16 hours and a temperature of 20°C ($\pm 2^\circ\text{C}$) were maintained throughout the growth period. Photos were taken of all treatments before termination of the experiment and qualitative observations of growth were made at regular intervals.

Preparation of plant and soil samples from greenhouse study.

At the end of 45 days, the aerial portion of the barley plants were harvested by replicate and immediately dried in a forced air oven at 70°C for 24 hours. Dry matter yield was determined and the vegetative material subsequently ground in a Waring blender. The ground plant material was wet ashed in a perchloric-nitric acid solution (Isaac and Kerber, 1971). Resultant plant extracts were brought to a uniform volume and total plant contents of Na, Ca, Mg, K, Al and Mn were analyzed using atomic absorption spectrophotometry. Methodology employed was as described by Isaac and Kerber (1971). A minor modification was the use of 2,000 ppm La (w/v) in the final dilution to act as a buffer in determination of Ca and Mg in lieu of a 1 percent La concentration suggested by Isaac and Kerber.

Immediately after termination of the greenhouse experiment, the soil was removed from each pot, screened to remove plant roots (undecomposed organic matter), and air dried. Subsamples from each replicate were subsequently oven dried and brought to equilibrium in a 1:2½ soil:water suspension. Soil reaction was determined in each soil solution using a glass electrode pH meter.

Statistical Analysis of Data

Quantitative data resulting from chemical analyses of the soils taken from the "Various Forms of N Trial" were subjected to analysis of variance to determine significance ($p \leq 0.05$, $p \leq 0.01$) and subsequently Duncan's Multiple Range Test was applied to determine significant differences among treatments. The same statistical procedures were employed to plant and soil composition data obtained from the greenhouse study.

Data from the paired sampling format of the "Fertility Test" were analyzed through application of a t-test. Significant differences were recorded.

Calculations of correlation coefficients for several specific soil and plant parameters were also performed.

RESULTS AND DISCUSSION

Soil Analysis Data from the "Various Forms of N Trial"

Introduction. Core samples were taken by replicate from the unfertilized Check as well as each of the areas treated with NH_4NO_3 , NH_2CONH_2 and $(\text{NH}_4)_2\text{SO}_4$. The thickness of the Ap horizon averaged approximately 10 cm and was sampled in 2.5 cm segments. Below the Ap, the Bnt horizon was sectioned into 5 cm segments from a depth of 10 to 30 cm. The depth at which the Csk horizon began was variable and was determined by testing for the presence of free CaCO_3 with dilute HCl. Once the depth of the Csk was identified, a section 5 cm above this point was retained as a sample. The total number of samples for each soil parameter, then, was nine. Soils from each sample depth were subsequently analyzed and the mean values for replicates of each of the N fertilizer treatments and Check were subjected to Duncan's New Multiple Range Test. Statistical differences were determined at $p \leq 0.05$.

A brief overview of the data makes it evident that a great deal of variability occurs for certain chemical characteristics among replicates at a particular depth. For example, data for extractable Na (10-15 cm), extractable Al (0-2.5 cm) and soluble Mn (5-7.5 cm) show range differences between means of the most extreme treatments in the order of 2.5, 5 and 5.75 times the absolute value of the lesser figures, respectively. Yet, the statistical analysis for each of these sets of data shows non-significance. Reports are documented of

significant variability in the chemistry and characteristics within Solonetzic areas occurring over short distances of several meters (Cairns, 1961; Peters, 1973). Pawluk (1973) found that the groundwater regime and its Na content varied dramatically over a radius of less than 30 m. Variance in the groundwater reflected the chemistry and productivity of a Solonetzic soil complex, which included a Duagh SiL. Substantial variability over short distances in Luvisolic soils has also been recorded (McCoy and Webster, 1977). Incongruities among replicates can effectively mask the effects of treatments added to ameliorate Solonetzic soils.

Cation Exchange Capacity (CEC). Generally the fertilizer treatments did not have an appreciable effect in altering CEC within the Ap and Bnt horizons. The only significant differences occurred for the 15-20 cm depth. The Check soil at this depth has a CEC that is significantly lower ($p \leq 0.05$) than that for either of the NH_4NO_3 or NH_2CONH_2 treatments. As well, $(\text{NH}_4)_2\text{SO}_4$ exhibits a significantly lower CEC as compared to NH_4NO_3 (Table 2). There is no significant variation with depth, although a weak tendency for CEC to decrease with depth is noted.

Electrical Conductivity (EC). Data indicate that the soils under study are not saline, and that treatments had a null effect on EC (Table 2). EC is generally highest at the uppermost sampling depth, and gradually decreases within the soil profiles.

Exchange acidity. Major differences are evident for exchange acidity. $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 treatments each resulted in significantly higher exchange acidity values ($p \leq 0.05$) as compared to the Check for the upper three depths within the Ap horizon (0-7.5 cm, Table 2). Also, $(\text{NH}_4)_2\text{SO}_4$ significantly increased exchange acidity over NH_2CONH_2 in these three uppermost depths. While there are no statistical differences between $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 at the surface sampling depth (0-2.5 cm), values are significantly dissimilar ($p \leq 0.05$) at both the 2.5-5 and 5-7.5 cm depths. NH_4NO_3 increased the exchange acidity as compared to NH_2CONH_2 in the Ap horizon within a band 0-7.5 cm, although not enough to be statistically significant. The same trend is noted for NH_2CONH_2 vs. Check.

The effects on exchange acidity rapidly decrease with depth for all treatments. NH_4NO_3 and NH_2CONH_2 give essentially the same values as the Check in the lower Ap horizon (7.5-10 cm). Although not significant, a degree of increased exchange acidity is noted with $(\text{NH}_4)_2\text{SO}_4$ into the upper part of the Bnt horizon (Figure 2). The convergence of values for exchange acidity as depth increases is an indication that causative factors for increase of this soil parameter are a result of topical additions made to the soil and the effects are the most prominent at the surface of the profile.

Soil pH. The comparative activity of H ions, as measured in a 1:2½ soil:water suspension, is influenced by the additions of N fertilizers. Generally, pH for the Check area shows a slight decline from the upper to lower Ap and upper Bnt of the soil profile (Table 3).

With increased depth, pH begins to rise rapidly below 20 cm and is near neutrality at a depth 5 cm above the Csk horizon. All treatments have pH values near neutrality at this depth (Figure 1). The rapid rise in soil pH in the lower regions of the profile may be a direct result of leaching of bases into the lower Bnt and Csk horizons.

$(\text{NH}_4)_2\text{SO}_4$, as compared to the other three treatments, significantly depressed soil pH at virtually all sampling depths from 0-15 cm ($p \leq 0.05$; Table 3). The only exceptions are samples taken at 2.5-5 cm and 5-7.5 cm. At these depths, $(\text{NH}_4)_2\text{SO}_4$ decreased pH relative to NH_4NO_3 , but differences are not significant. NH_4NO_3 caused a pH significantly lower than that in the Check at a depth of 0-5 cm and the same trend persists into the lower Ap. NH_2CONH_2 produced slightly depressed pH values for the Ap horizon as compared to the Check, although none of the differences are statistically significant ($p \leq 0.05$).

Additions of NH_4NO_3 , NH_2CONH_2 and $(\text{NH}_4)_2\text{SO}_4$ over a period of ten years had a tendency to depress soil pH in the Ap horizon of a Duagh Sil. As predicted from literature references, $(\text{NH}_4)_2\text{SO}_4$ had significantly more potential to acidify soils than the other two N sources involved in this trial. The pH effects of $(\text{NH}_4)_2\text{SO}_4$ are significant into the upper Bnt horizon (Table 3). The degree of acidification decreases from the surface to the lower regions of the profile, indicating that the depressions in the pH values are resultant of surface applications of N fertilizers. Overall, the various forms of N had a net effect of decreasing pH in a sequence $(\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{NO}_3 > \text{NH}_2\text{CONH}_2$, and this followed trends suggested in the literature. Also, as expected, increases in H ion activity showed the same trends

as exchange acidity (Figures 1 and 2), although differences in pH are measurable slightly deeper into the soil profile.

Extractable Al. The highest levels for NH_4OAc -extractable Al (pH 6.5) are recorded for the $(\text{NH}_4)_2\text{SO}_4$ treatment and are considerably higher than for the Check throughout the Ap horizon (Table 3). The trend continues into the upper 5 cm of the Bnt, although differences are generally not significant past the Ap horizon for all treatments ($p \leq 0.05$). Figure 3 elucidates that the pattern for convergence follows that for soil reaction. A strongly negative correlation coefficient ($p \leq 0.01$) exists for pH vs. Al (Table 4). This implies that as pH increases, extractable Al is expected to decline, and thus follows trends suggested in the literature (Sivasubramaniam and Talibudeen, 1972). The pH levels for the fertilizer treatments and Check throughout most of the Ap and upper Bnt horizons are at or near values expected to cause significant concentrations of trivalent Al within the soil system (Kamprath, 1970; Hoyt, 1977).

Soil Mn. $(\text{NH}_4)_2\text{SO}_4$ additions lead to significant ($p \leq 0.05$) increases of extractable Mn in the region 0-7.5 cm as compared to the Check, NH_4NO_3 and NH_2CONH_2 . This trend continues into the lower part of the Ap horizon, but is not significant (Table 3). NH_4NO_3 also caused some increase in extractable Mn, although the magnitude is much less and the depths to which effects are noticed are more shallow than for $(\text{NH}_4)_2\text{SO}_4$. The decrease of extractable Mn within $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 treatments as depth increases in the Ap horizon is rapid and clearly evident (Figure 4). Soluble Mn follows the same fertilizer

induced response pattern of extractable Mn. However, differential effects are confined to a more shallow depth in the case of soluble Mn. A significant negative correlation ($p \leq 0.01$) exists between pH and extractable Mn, although the coefficient is of less magnitude than the relationship between pH and extractable Al (Table 4). Extractable Mn and Al are closely correlated.

Soil K. Applications of NH_2CONH_2 significantly depressed extractable K as compared to the Check at depths from 2.5-15 cm. NH_4NO_3 produced the same response, although significant differences are not noted until the 5 cm depth (Table 3). Soluble K is significantly depressed by NH_2CONH_2 vs. Check at 2.5-7.5 cm (Table 5). NH_4NO_3 had generally no significant effects on soluble K levels with respect to the other treatments. $(\text{NH}_4)_2\text{SO}_4$ resulted in the highest extractable K values from the surface of the profile and the differences as compared to the Check are significant from 5-10 cm ($p \leq 0.05$). Extractable K drops rapidly with depth in the Ap and stabilizes in the Bnt horizon (Figure 5). It is probable that extractable K was released from soil minerals in significant quantities under the influence of the acidification developed by $(\text{NH}_4)_2\text{SO}_4$. Extractable K is significantly correlated to soil pH.

Soil Na. Levels of extractable Na were significantly reduced by $(\text{NH}_4)_2\text{SO}_4$ at 0-2.5 cm compared to the Check and NH_2CONH_2 . The trend for $(\text{NH}_4)_2\text{SO}_4$ to lower extractable Na throughout the Ap and Bnt horizons to a depth of at least 20 cm is apparent (Figure 6). However, the decreases are not great enough to overcome the variability

within replicates and the differences remain non-significant ($p \leq 0.05$; Table 6). NH_4NO_3 also appears to have a tendency to reduce Na although its effects are less than for $(\text{NH}_4)_2\text{SO}_4$. Data for soluble Na exhibit the same trends as for extractable Na, although none of the differential responses are significant (Table 5). Extractable Na is highly correlated with pH and also significantly related to extractable Ca and Mg (Table 4). Negative significant correlations ($p \leq 0.01$) exist between extractable Na and each of extractable K, Al, and Mn.

Soil Ca. As in the case of extractable Na, $(\text{NH}_4)_2\text{SO}_4$ resulted in a significant reduction ($p \leq 0.05$) of Ca in the uppermost sampling depth (Table 6). A marked depression of extractable Ca in the $(\text{NH}_4)_2\text{SO}_4$ treatment as compared to the Check persists into the Bnt, to an approximate depth of 15 cm, although differences are not significant. Extractable Ca in the Check decreases with depth. On the other hand, Ca levels for $(\text{NH}_4)_2\text{SO}_4$ are very low at depths near the surface and increase with depth (Figure 7). This suggests that Ca has been mobilized and moved from the upper portions of the profile. Some minor decreases of extractable Ca are noted in the NH_4NO_3 treatment as compared to the Check, but these are less than those in the $(\text{NH}_4)_2\text{SO}_4$ treatment. An interesting discovery is that commencing from 5 cm, NH_4NO_3 significantly raises the levels of soluble Ca throughout the profiles examined. The ability of NH_4NO_3 to increase the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in a Duagh SiL is recorded (Carter et al., 1977). It is not thought, however, that this salt naturally exists in the Ap and Bnt horizons in this soil; yet NH_4NO_3 was effective in

raising soluble Ca. Extractable Ca is highly correlated with soil pH as well as negatively related to exchangeable Al (Table 4).

Extractable Ca:Na ratio. Carter et al. (1977) reported that additions of NH_4NO_3 plus $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ increased the extractable Ca:Na ratio over NH_4NO_3 alone. There is some speculation, however, that NH_4 may have a direct benefit in increasing the Ca:Na ratio (van Schaik and Cairns, 1967; Ryzhova and Gorbunov, 1975). In the trial under study, $(\text{NH}_4)_2\text{SO}_4$ and NH_2CONH_2 selectively leached Ca from the upper portions of the Ap horizon and thus undesirably lowered the Ca:Na ratio as compared to the Check. Selective leaching of Ca continued below this depth with NH_2CONH_2 and decreased Ca:Na ratios are found to a depth of 5 cm above the Csk (Table 6). The Ca:Na ratios for $(\text{NH}_4)_2\text{SO}_4$, on the other hand, become similar to those for the Check in the lower Ap (5-10 cm) and show marginal improvement throughout the Bnt horizon (Table 6), suggesting preferential leaching of Na. NH_4NO_3 seems to closely parallel the Check in terms of Ca:Na ratio.

Soil Mg. Of the four treatments, $(\text{NH}_4)_2\text{SO}_4$ has the greatest effect in reducing extractable Mg (Table 6). Mg was significantly decreased by $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 at the 0-5 cm depth. Data show that values for extractable Mg for the Check as well as the NH_2CONH_2 and NH_4NO_3 treatments converge rapidly (Figure 8). At a depth of 5-7.5 cm there are no statistically significant differences between any of the treatments and past 10-15 cm (Bnt and lower) values of Mg for all treatments are very similar (Figure 8). Soluble Mg is

significantly lowered by $(\text{NH}_4)_2\text{SO}_4$ to a depth of 7.5 cm, while other treatments show no significant differences. Extractable Mg has a significant correlation ($p \leq 0.01$) with soil pH and Ca and a strongly significant negative correlation with Al (Table 4).

High Rates of NH_4NO_3 vs. Check Field Experiment: Soil Analysis Data

Introduction. NH_4NO_3 was applied annually to an established bromegrass (Bromus inermis) and Kentucky bluegrass (Poa pratensis L.) sod at a rate of 300 kg/ha N per year for 12 years commencing in 1961. Bromegrass responded vigorously to the applications of N fertilizer and rapidly became the prominent species in the NH_4NO_3 treated area. Over the first five years, forage yield was markedly higher for the NH_4NO_3 treatment and the root mass nearly doubled during the same period of time (Cairns et al., 1967). Up to the time of sampling in 1973, the positive yield response to N fertilizer continued (Dr. R. R. Cairns, personal communication). Other reports of yield responses to high rates of NH_4NO_3 are documented. In the greenhouse, NH_4NO_3 at rates of 300 ppm and 600 ppm N significantly increased the yield of barley and improved the hydraulic conductivity of a Solonetzic soil (Cairns, 1972a).

Twelve years after this field trial was established, soils were sampled at several fixed depths throughout the Ap and Bnt horizons. The top 10 cm of the Csk was also sampled and retained for chemical analysis. Depth to the Csk was somewhat variable, but generally ranged from 25 to 30 cm. Profile development was found to be to a

Table 2. Chemistry of a Duagh Sil: various forms of N applied; cation exchange capacity; electrical conductivity; exchange acidity; and soluble Mn at several fixed profile depths

Depth (cm)										
Treatment	0-2.5*	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0	15.0-20.0	20.0-25.0	25.0-30.0	"x"	
Cation Exchange Capacity (meq/100 g)										
Check	36.94	34.38	33.63	33.20	29.87	27.36 ^a	31.02	32.42	28.54	
NH ₄ NO ₃	33.90	31.11	31.66	33.69	33.56	36.01 ^c	34.46	31.70	30.28	
NH ₂ CONH ₂	35.94	34.19	34.90	33.92	31.84	33.49 ^{bc}	34.02	29.18	32.93	
(NH ₄) ₂ SO ₄	34.37	32.06	31.99	31.53	28.93	28.66 ^{ab}	29.52	29.60	30.60	
Electrical Conductivity (mmhos/cm)										
Check	0.44	0.29	0.27	0.25	0.19	0.16	0.14	0.14	0.20	
NH ₄ NO ₃	0.47	0.26	0.19	0.18	0.14	0.10	0.09	0.10	0.16	
NH ₂ CONH ₂	0.47	0.25	0.20	0.19	0.15	0.12	0.12	0.12	0.26	
(NH ₄) ₂ SO ₄	0.39	0.21	0.21	0.22	0.17	0.15	0.14	0.15	0.20	

Table 2. (continued)

		Depth (cm)							
Treatment	0.2-5*	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0	15.0-20.0	20.0-25.0	25.0-30.0	"x"
<u>Exchange Acidity (meq/100 g)</u>									
Check	15.91 ^a	16.44 ^a	15.17 ^a	16.69	13.13	10.22	8.78	6.54	3.79
NH ₄ NO ₃	27.22 ^{bc}	23.47 ^b	19.11 ^b	16.36	12.40	11.64	9.52	8.65	4.58
NH ₂ CONH ₂	18.99 ^{ab}	19.24 ^{ab}	18.90 ^{ab}	17.66	13.46	10.41	9.53	7.84	3.33
(NH ₄) ₂ SO ₄	35.59 ^c	30.02 ^c	24.79 ^c	22.24	13.96	10.52	9.74	9.06	4.61
<u>Soluble Mn (ppm)</u>									
Check	3.96 ^a	5.34 ^{ab}	5.08	4.92	2.02	0.74	0.69	0.59	0.35
NH ₄ NO ₃	17.83 ^c	10.03 ^{bc}	1.63	1.83	0.61	0.27	0.27	0.21	0.34
NH ₂ CONH ₂	5.10 ^{ab}	2.92 ^a	2.40	2.40	0.55	0.29	0.19	0.18	0.20
(NH ₄) ₂ SO ₄	14.22 ^{bc}	14.32 ^c	9.37	4.04	1.56	0.66	0.48	0.24	0.19

"x" represents a sample depth 5 cm above the Csk horizon.

* For each soil parameter, differing letters following values at a particular depth indicate significant differences (p ≤ 0.05).

Table 3. Chemistry of a Duagh Sil; various forms of N applied; pH; extractable Al, Mn and K at several fixed profile depths

		Depth (cm)							
Treatment		0-2.5*	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0	15.0-20.0	20.0-25.0	25.0-30.0 "x"
<u>pH (1:2½ Soil:Water Ratio)</u>									
Check		6.00 ^c	5.76 ^c	5.65 ^b	5.64 ^b	5.62 ^b	5.37	5.69	6.77 7.11
NH ₄ NO ₃		4.97 ^b	4.89 ^{ab}	5.27 ^{ab}	5.45 ^b	5.53 ^b	5.57	5.63	6.12 6.87
NH ₂ CONH ₂		5.67 ^c	5.34 ^{bc}	5.40 ^b	5.47 ^b	5.58 ^b	5.80	6.05	6.07 7.19
(NH ₄) ₂ SO ₄		4.50 ^a	4.35 ^a	4.79 ^a	5.06 ^a	5.14 ^a	5.29	5.45	5.65 6.74
<u>Extractable Al (ppm)</u>									
Check		3.15	5.53 ^a	5.66 ^a	4.81 ^a	4.84	5.14	4.57 ^{ab}	4.50 0.00
NH ₄ NO ₃		12.28	8.19 ^a	6.54 ^a	6.77 ^{ab}	5.53	5.11	4.09 ^a	3.61 0.00
NH ₂ CONH ₂		10.23	10.10 ^{ab}	9.89 ^{ab}	8.54 ^{bc}	7.04	4.71	5.46 ^b	4.98 0.00
(NH ₄) ₂ SO ₄		15.38	15.86 ^b	11.74 ^b	10.75 ^c	8.41	5.35	5.10 ^b	4.39 0.00

Table 3. (continued)

Treatment	Depth (cm)									"x"
	0-2.5*	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0	15.0-20.0	20.0-25.0	25.0-30.0		
<u>Extractable Mn (ppm)</u>										
Check	44.07 ^a	44.61 ^a	43.99 ^a	40.96	30.90	11.53	7.71	6.82	10.56	
NH ₄ NO ₃	76.54 ^a	68.42 ^b	35.27 ^a	28.53	12.41	5.52	5.46	5.12	4.23	
NH ₂ CONH ₂	55.80 ^a	45.84 ^a	39.77 ^a	37.36	14.80	10.78	7.57	6.07	5.86	
(NH ₄) ₂ SO ₄	120.64 ^b	93.16 ^c	83.50 ^b	48.65	15.67	5.72	5.17	7.67	6.87	
<u>Extractable K (meq/100 g)</u>										
Check	2.59	1.66 ^{bc}	1.23 ^b	1.02 ^b	0.81 ^b	0.64	0.69	0.74	0.70	
NH ₄ NO ₃	2.88	1.39 ^{ab}	0.81 ^a	0.56 ^a	0.52 ^a	0.64	0.66	0.65	0.55	
NH ₂ CONH ₂	2.26	1.15 ^a	0.82 ^a	0.62 ^a	0.54 ^a	0.64	0.66	0.68	0.61	
(NH ₄) ₂ SO ₄	4.53	1.92 ^c	1.52 ^c	1.15 ^c	0.78 ^b	0.74	0.77	0.74	0.69	

"x" represents a sample depth 5 cm above the Csk horizon.

* For each soil parameter, differing letters following values at a particular depth indicate significant differences (p ≤ 0.05).

Table 4. Correlation of specific soil parameters including pH
 and extractable cations for various forms of N applied
 to a Duagh SiL

	pH	Na	K	Ca	Mg	Al	Mn
pH	--						
Na	0.86**	--					
K	-0.46**	-0.44**	--				
Ca	0.85**	0.59**	-0.30	--			
Mg	0.75**	0.73**	-0.57**	0.70**	--		
Al	-0.89**	-0.71**	0.62**	-0.83**	-0.80**	--	
Mn	-0.67**	-0.63**	0.84**	-0.55**	-0.86**	0.82**	--

** Correlations significant at $p \leq 0.01$.

* Correlations significant at $p \leq 0.05$.

(36 pairs of data)

Table 5. Chemistry of a Duagh SiL: various forms of N applied; soluble Na, Ca, Mg and K at several fixed profile depths

		Depth (cm)							
Treatment	0-2.5*	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0	15.0-20.0	20.0-25.0	25.0-30.0	"x"
<u>Soluble Na (meq/100 g)</u>									
Check	1.51	1.53	1.67	2.04	2.24	2.53	2.88	3.36	4.50
NH ₄ NO ₃	1.43	0.77	1.11	1.68	2.07	2.38	2.83	3.32	4.79
NH ₂ CONH ₂	1.67	1.60	2.06	2.81	3.05	3.31	3.60	3.66	9.21
(NH ₄) ₂ SO ₄	1.09	0.74	1.05	1.59	1.33	1.47	2.04	2.72	3.86
<u>Soluble Ca (meq/100 g)</u>									
Check	0.45	0.39	0.41 ^a	0.43 ^b	0.32 ^a	0.29 ^a	0.26 ^b	0.25 ^c	0.14 ^a
NH ₄ NO ₃	0.63	0.65	0.68 ^b	0.68 ^c	0.59 ^b	0.50 ^b	0.51 ^c	0.53 ^d	0.63 ^b
NH ₂ CONH ₂	0.90	0.29	0.28 ^a	0.24 ^a	0.23 ^a	0.26 ^a	0.18 ^{ab}	0.17 ^b	0.16 ^a
(NH ₄) ₂ SO ₄	0.38	0.34	0.32 ^a	0.34 ^{ab}	0.19 ^a	0.12 ^a	0.09 ^a	0.05 ^a	0.14 ^a

Table 5. (continued)

Treatment	Depth (cm)								"x"
	0-2.5*	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0	15.0-20.0	20.0-25.0	25.0-30.0	
<u>Soluble Mg (meq/100 g)</u>									
Check	0.39 ^b	0.29 ^b	0.25 ^b	0.25	0.25	0.08	0.07	0.07 ^b	0.09
NH ₄ NO ₃	0.36 ^b	0.29 ^b	0.23 ^b	0.26	0.11	0.01	0.01	0.01 ^a	0.15
NH ₂ CONH ₂	0.48 ^b	0.22 ^b	0.16 ^{ab}	0.14	0.06	0.05	0.03	0.02 ^a	0.06
(NH ₄) ₂ SO ₄	0.07 ^a	0.03 ^a	0.09 ^a	0.16	0.11	0.04	0.02	0.07 ^b	0.11
<u>Soluble K (meq/100 g)</u>									
Check	0.57	0.29 ^b	0.19 ^b	0.15	0.09	0.05	0.05	0.05 ^a	0.06
NH ₄ NO ₃	0.72	0.24 ^{ab}	0.14 ^{ab}	0.12	0.10	0.10	0.08	0.08 ^b	0.09
NH ₂ CONH ₂	0.52	0.20 ^a	0.11 ^a	0.08	0.08	0.09	0.07	0.08 ^b	0.11
(NH ₄) ₂ SO ₄	0.60	0.27 ^b	0.20 ^b	0.16	0.10	0.09	0.08	0.12 ^c	0.10

"x" represents a sample depth 5 cm above the Csk horizon.

* For each soil parameter, differing letters following values at a particular depth indicate significant differences ($p \leq 0.05$).

Table 6. Chemistry of a Duagh SiL: various forms of N applied; extractable Na, Ca, Mg and Ca:Na ratios at several fixed profile depths

		Depth (cm)							
Treatment	0-2.5*	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0	15.0-20.0	20.0-25.0	25.0-30.0	"x"
<u>Extractable Na (meq/100 g)</u>									
Check	5.73 ^b	5.32	5.37	6.05	6.17	7.71	9.79	11.21	17.53
NH ₄ NO ₃	4.72 ^{ab}	3.66	4.33	5.19	5.94	7.66	10.23	13.17	18.69
NH ₂ CONH ₂	5.10 ^b	5.44	6.38	8.32	10.76	13.84	14.63	15.68	24.26
(NH ₄) ₂ SO ₄	3.83 ^a	3.05	3.52	3.81	4.29	6.70	7.54	7.88	11.53
<u>Extractable Ca (meq/100 g)</u>									
Check	19.79 ^b	16.80	16.51	16.66	15.06	13.67	15.63	16.60	20.19
NH ₄ NO ₃	14.88 ^b	13.15	15.02	14.95	14.12	15.30	16.16	17.95	25.52
NH ₂ CONH ₂	17.78 ^b	13.66	11.97	13.80	12.73	15.75	14.41	14.17	18.34
(NH ₄) ₂ SO ₄	8.36 ^a	7.22	10.68	10.67	12.38	13.79	15.27	15.66	19.39

Table 6. (continued)

Treatment	Depth (cm)									"x"
	0-2.5*	2.5-5.0	5.0-7.5	7.5-10.0	10.0-15.0	15.0-20.0	20.0-25.0	25.0-30.0		
<u>Extractable Mg (meq/100 g)</u>										
Check	6.01 ^c	4.82 ^c	4.75	4.80	4.54	5.09	6.03	6.63	6.12	
NH ₄ NO ₃	3.06 ^b	2.81 ^{ab}	3.76	4.20	4.95	6.03	6.28	6.80	7.08	
NH ₂ CONH ₂	5.29 ^c	4.50 ^{bc}	4.61	4.89	4.87	6.17	6.36	6.47	7.14	
(NH ₄) ₂ SO ₄	1.71 ^a	1.70 ^a	2.31	3.16	4.87	5.47	6.39	6.02	4.15	
<u>Ca:Na (Extractable)⁺</u>										
Check	3.45	3.15	3.08	2.75	2.44	1.77	1.60	1.48	1.15	
NH ₄ NO ₃	3.15	3.59	3.47	2.88	2.38	2.00	1.58	1.36	1.36	
NH ₂ CONH ₂	3.49	2.51	1.88	1.66	1.18	1.14	0.98	0.90	0.76	
(NH ₄) ₂ SO ₄	2.18	2.37	3.03	2.80	2.88	2.06	2.02	1.99	1.68	

"x" represents a sample depth 5 cm above the Csk horizon.

* For each soil parameter, differing letters following values at a particular depth indicate significant differences ($p \leq 0.05$).

+ Duncan's new multiple range test for statistical significance was not performed on Ca:Na ratio data.

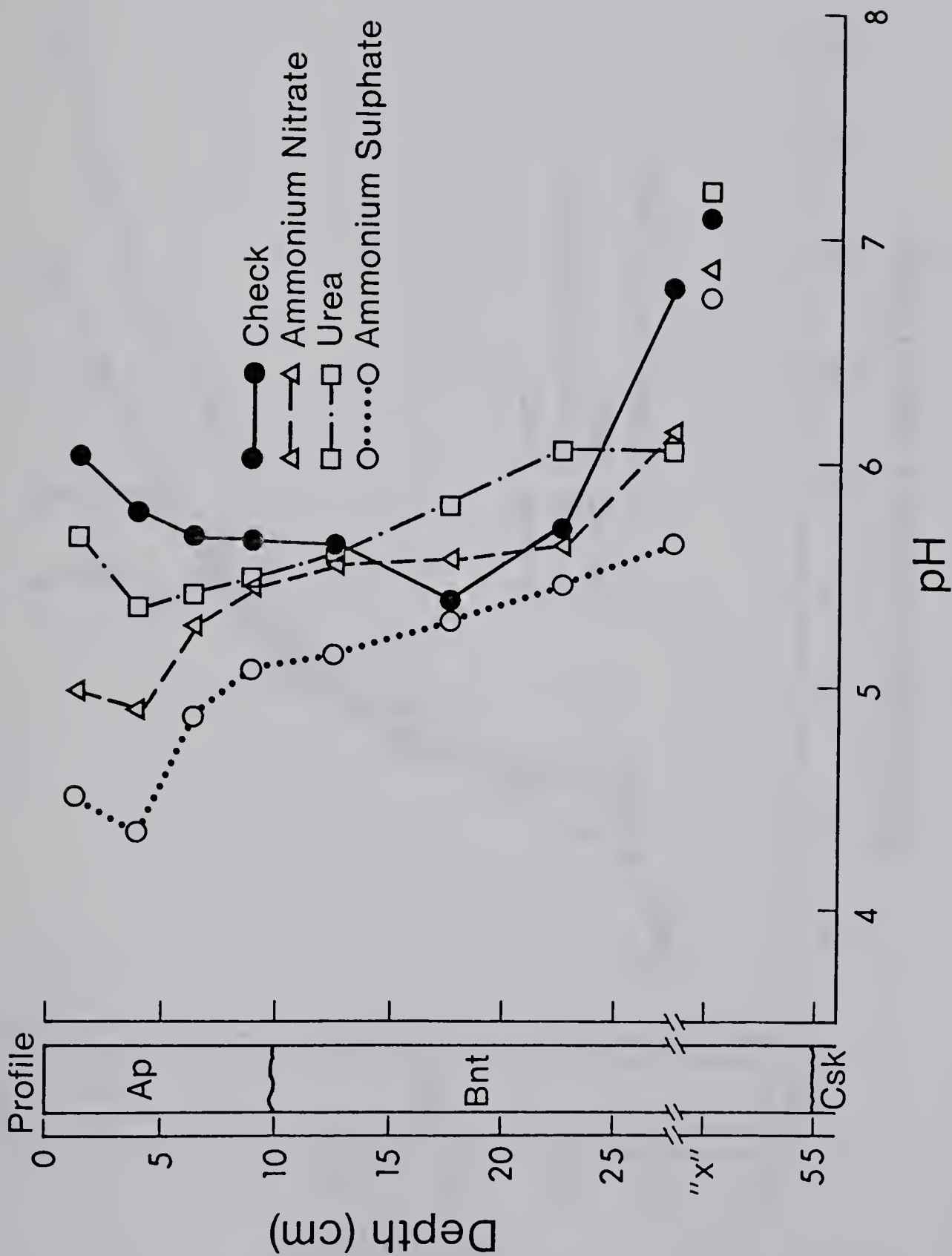


Figure 1. Effects of several N fertilizers on soil pH of Ap and Bnt horizons of a Duagh Sil.

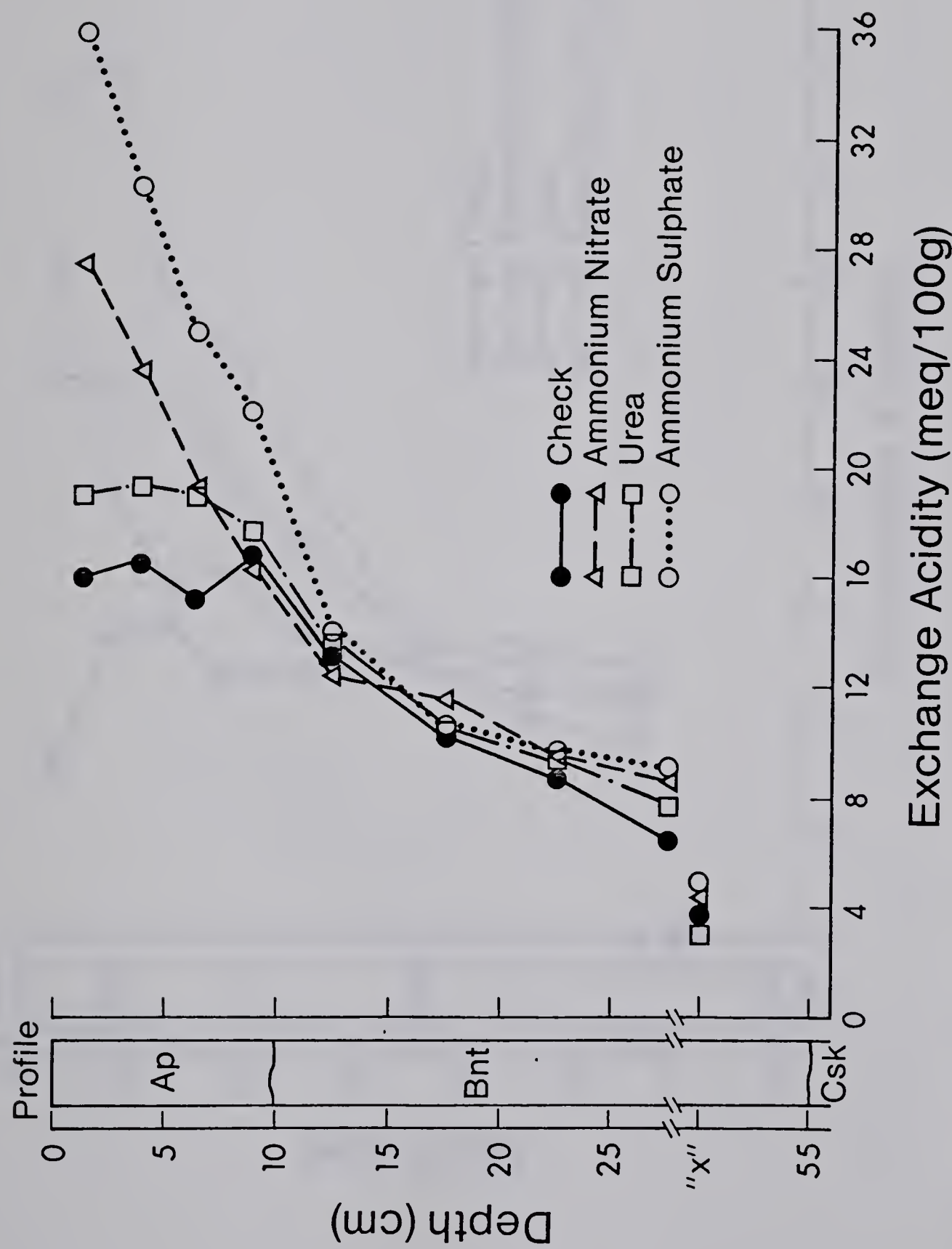


Figure 2. Effects of several N fertilizers on exchange acidity of Ap and Bnt horizons of a Duagh SiL.

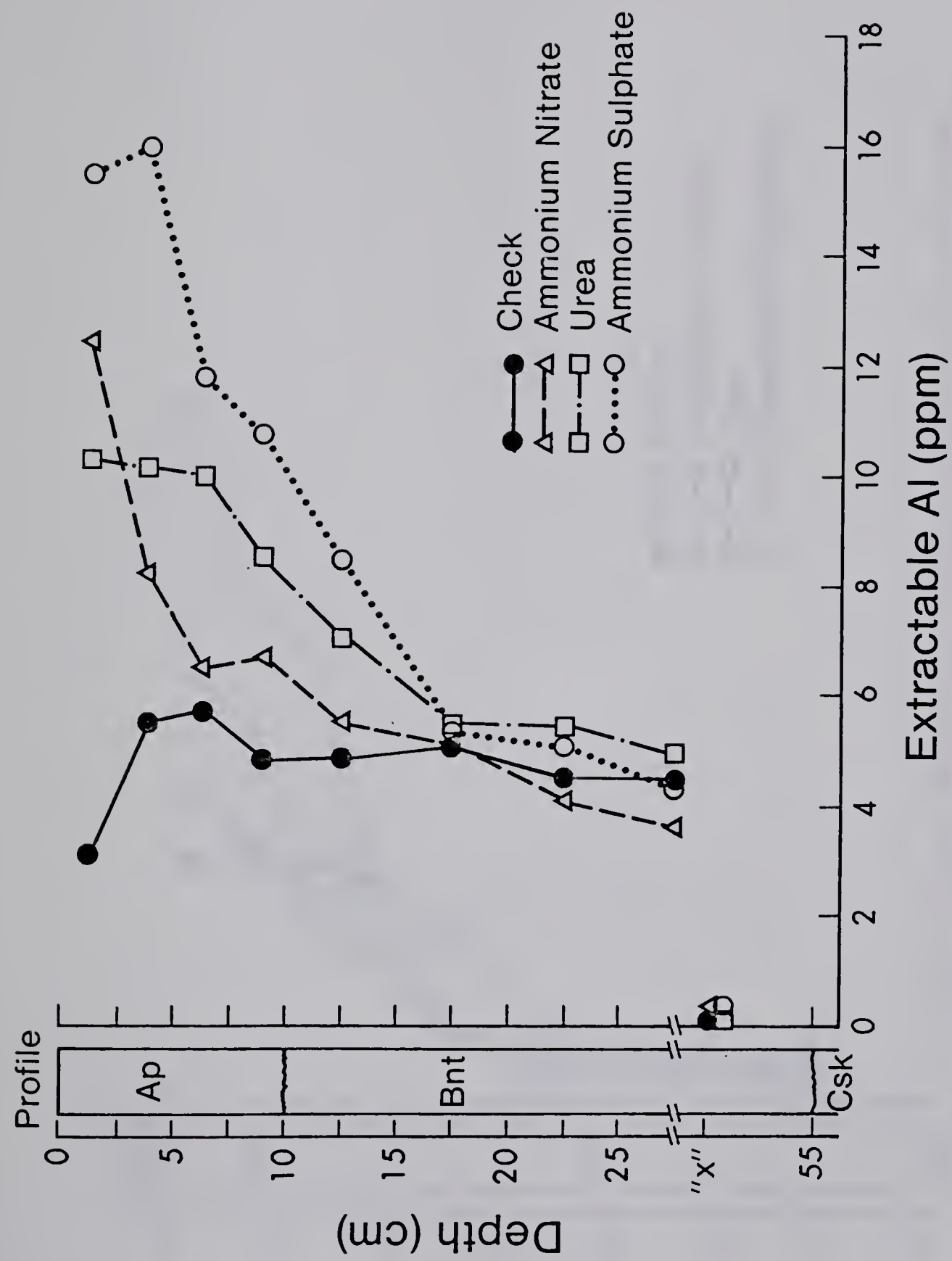


Figure 3. Effects of several N fertilizers on extractable Al of Ap and Bnt horizons of a Duagh SiL.

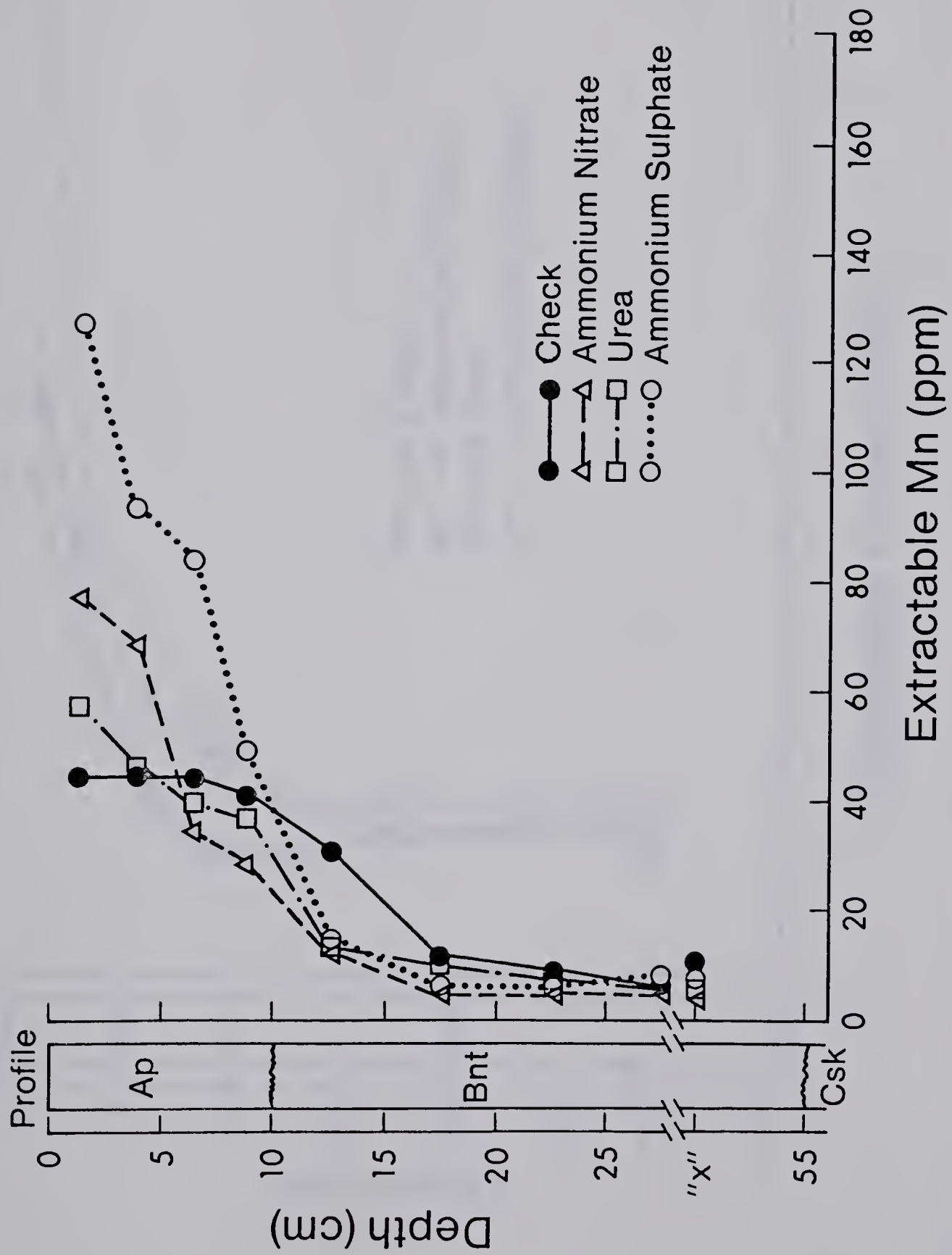


Figure 4. Effects of several N fertilizers on extractable Mn of Ap and Bnt horizons of a Duagh SiL.

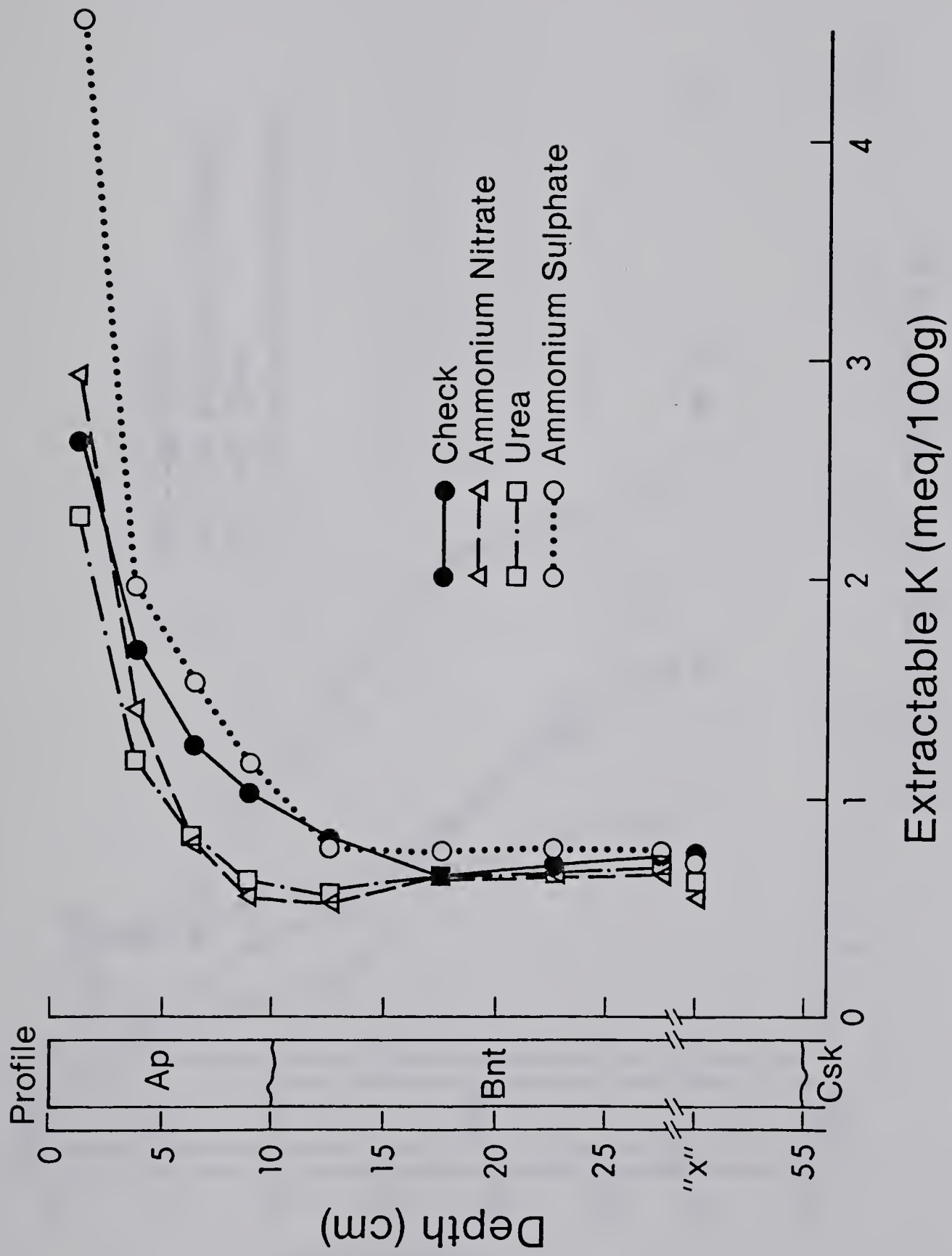


Figure 5. Effects of several N fertilizers on extractable K of Ap and Bnt horizons of a Duagh SiL.

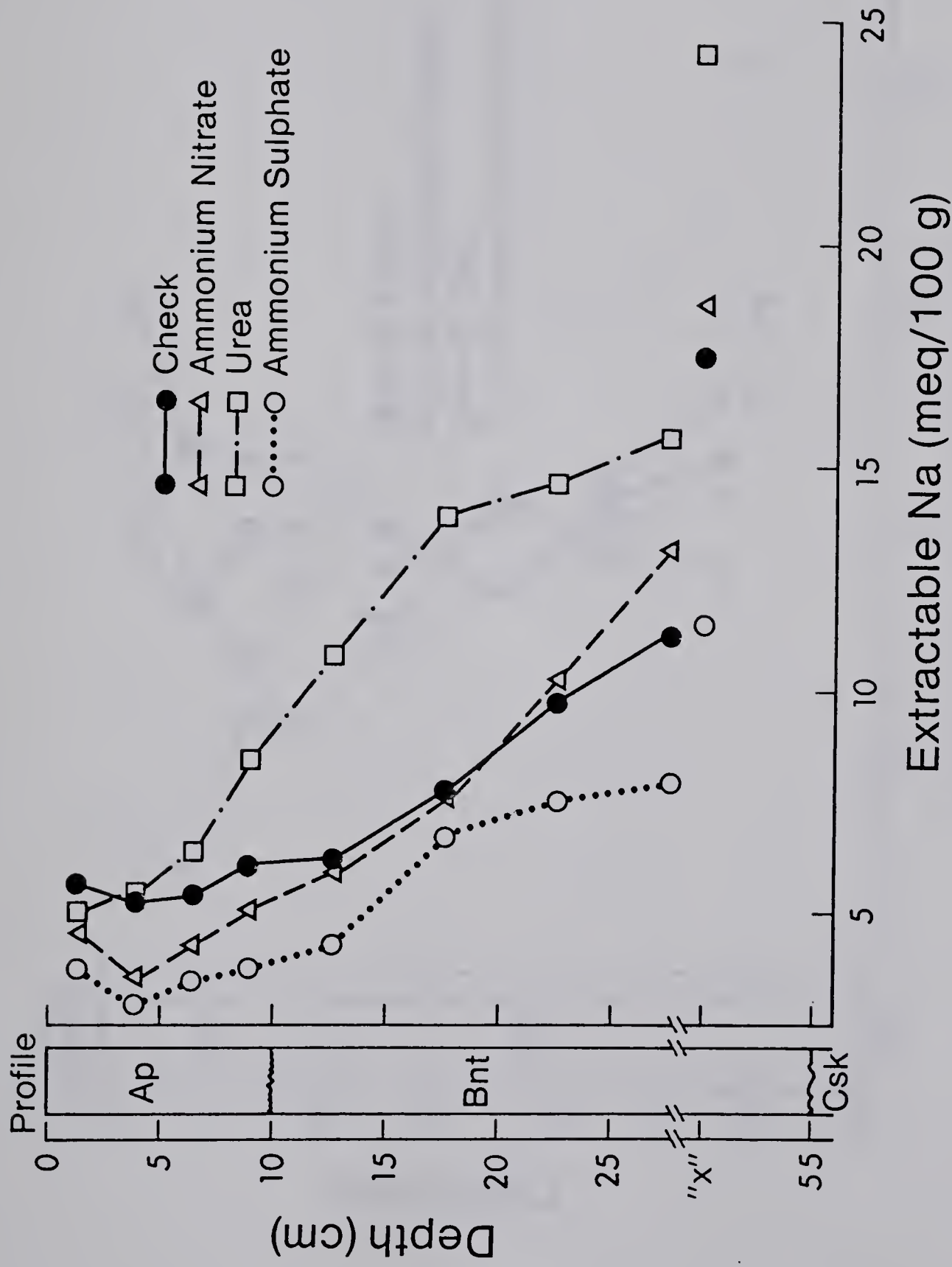


Figure 6. Effects of several N fertilizers on extractable Na of Ap and Bnt horizons of a Duagh Sil.

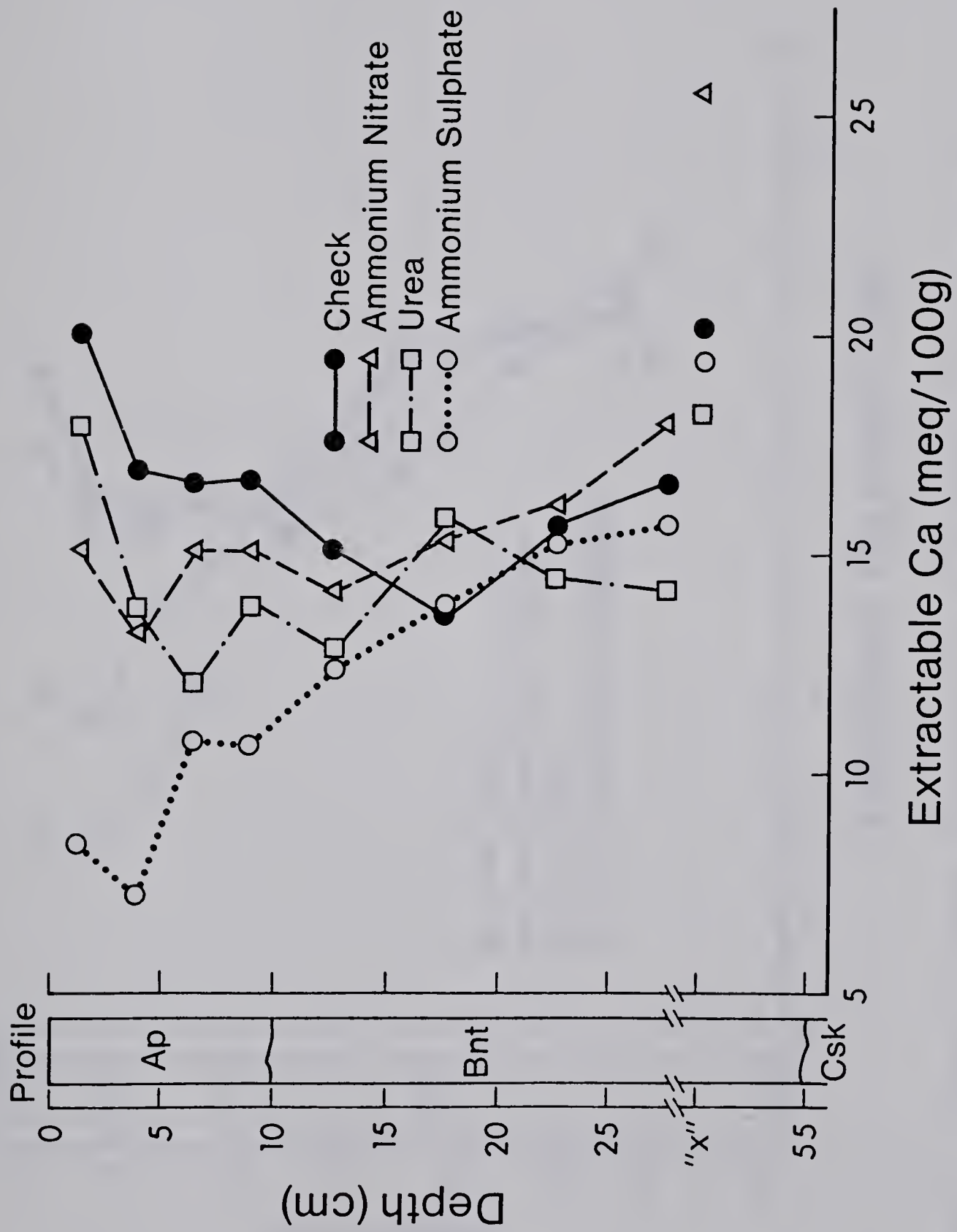


Figure 7. Effects of several N fertilizers on extractable Ca of Ap and Bnt horizons of a Duagh Sil.

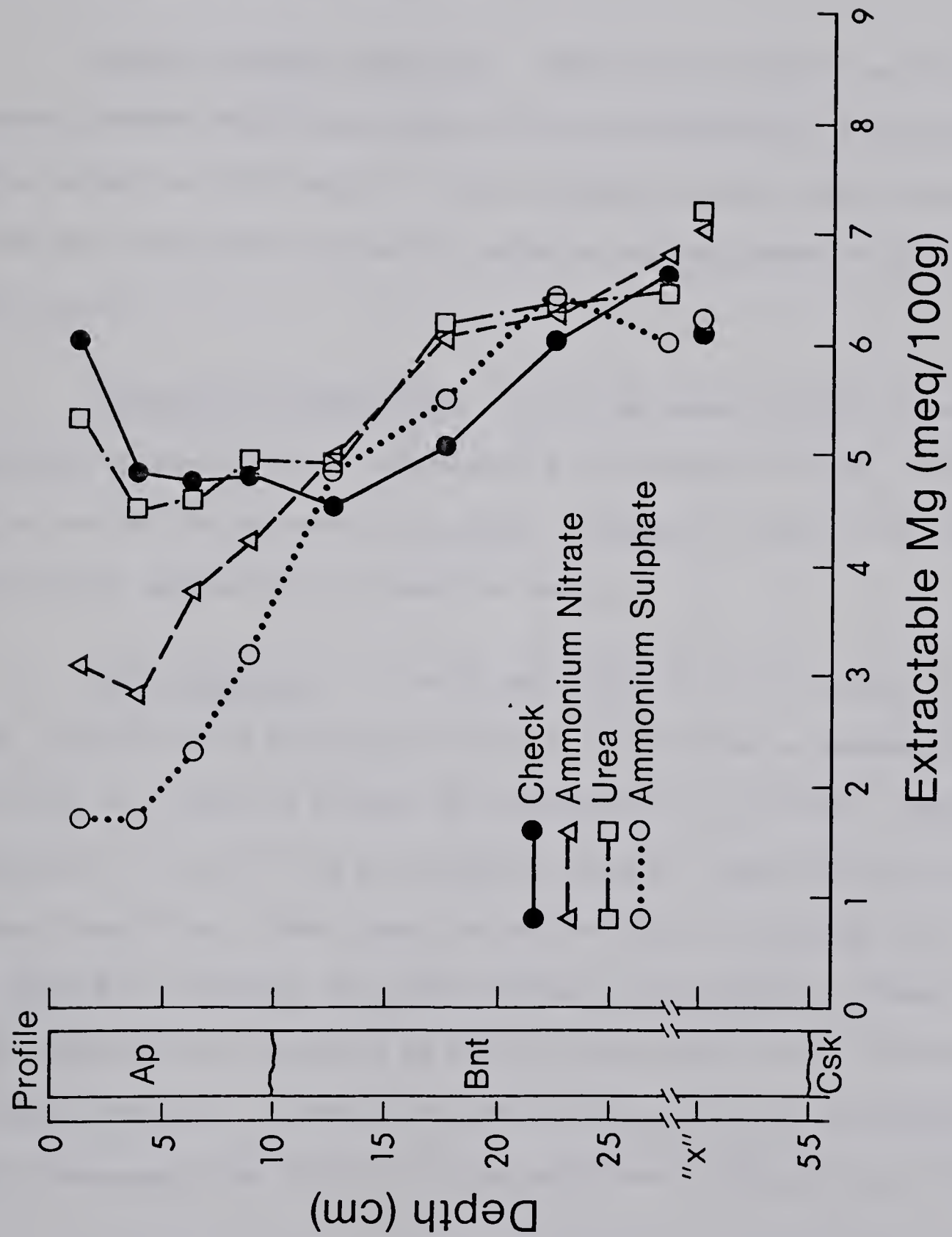


Figure 8. Effects of several N fertilizers on extractable Mg of Ap and Bnt horizons of a Duagh SiL.

lesser depth than that in the "Various Forms of N Trial" discussed previously. At the same time, the high degree of replicate variability found for several soil parameters within the "Various Forms of N Trial" is not encountered in the experiment.

Cation exchange capacity. There are no significant differences between NH_4NO_3 and Check and it is concluded the fertilizer has no effect on CEC (Table 7). CEC is highest in the lower section of the Bnt horizon and may be indicative of an enrichment of clay in this region.

Electrical conductivity. As is the case with CEC, electrical conductivity appears wholly unaffected by additions of NH_4NO_3 (Table 8). The Ap and Bnt horizons are non-saline, although EC does rise in the Csk horizon, indicating a presence of salts.

Soil reaction. T tested data show that applications of NH_4NO_3 significantly depressed soil pH (1:2½ soil: water suspension) in the Ap and upper Bnt horizon of the Duagh SiL ($p \leq 0.01$). However, differences in soil pH are not observed below the upper Bnt horizon (deeper than 17 cm). Soil reaction for the Check is alkaline from the upper Bnt throughout the lower portion of the profile. Though pH is significantly depressed by NH_4NO_3 in the upper Bnt, soil reaction is near neutrality. In the Ap horizon, however, soil pH is significantly depressed from 6.20 to 4.66 by additions of NH_4NO_3 ($p \leq 0.01$).

Exchange acidity. As expected, NH_4NO_3 significantly increased the exchange acidity in the Ap horizon ($p \leq 0.01$) and

significant differences persist throughout the Bnt horizon, to a depth of 27 cm (Table 7). The magnitude of differences between treatment and Check decreases dramatically from the Ap to the Bnt and Csk horizons.

Extractable Al. In the Ap horizon, more than twice the level of extractable Al is found in the NH_4NO_3 treatment, as compared to the Check (Table 7). Below the Ap, extractable Al decreased rapidly in the NH_4NO_3 treated profile; and levels for Al are low throughout the Bnt and Csk horizons. Analysis of data for pH and extractable Al results in a highly significant negative correlation coefficient in the Ap horizon, while there are no significant correlations at lower depths (Table 9).

Soil Mn. Extractable Mn is significantly higher ($p \leq 0.01$) for NH_4NO_3 than for the Check in the Ap horizon (Table 9). In the lower horizons, extractable Mn decreases rapidly and differences become non-significant. Soluble Mn follows basically the same pattern down the soil profile. As in the case of Al, extractable Mn has a strong negative correlation with pH in the Ap horizon, but the relationship does not continue into any of the lower horizons (Table 9). Mn and Al are also significantly correlated in the Ap horizon ($p \leq 0.01$).

Soil K. NH_4NO_3 effectively depressed extractable K in the Ap and Bnt horizons. Levels of K decrease with increasing depth within the profile (Table 7). Differences occur for soluble K in the upper Bnt for some inexplicable reason. Treatment effects are noted

deep into the Bnt horizon for extractable K, and significant correlations ($p \leq 0.01$) with pH are recorded in the Ap and upper Bnt horizons.

Soil Na. Extractable Na increases with depth within the soil profile (Table 7). NH_4NO_3 significantly decreased extractable and soluble Na within the region 0-17 cm (Ap and upper Bnt horizons). There is no net accumulation of Na in the lower Bnt horizon for the NH_4NO_3 treatment, even though significant leaching has occurred in the Ap and upper Bnt horizons. This implies that Na has been mobilized, has moved through the Bnt and into the lower depths of the Csk horizon. Once desorbed from the exchange complex, Na can have a high downward mobility in a Duagh SiL (van Schaik and Cairns, 1969). Significant correlations exist between pH and extractable Na in the Ap and upper Bnt horizons (Table 9).

Soil Ca. NH_4NO_3 significantly decreased extractable Ca within the Ap horizon (Table 7). However, deeper in the profile, a net gain in extractable Ca occurs in the upper and lower Bnt, although differences between Check and NH_4NO_3 are not significant. A slight increase of Ca in the NH_4NO_3 treatment over the Check suggests that Ca leached from the surface horizon accumulated in the Bnt. Increases of Ca in the Bnt horizon are collectively nearly equal to the amounts leached from the upper horizon. Extractable Ca and soil pH are significantly correlated in the Ap horizon ($p \leq 0.01$) and a weaker, negative relationship ($p \leq 0.05$) between the same two parameters exists in the upper Bnt. NH_4NO_3 dramatically increased soluble Ca

in the Ap horizon ($p \leq 0.01$), although the significant effect for increasing soluble Ca throughout the entire profile does not exist as was the case of lower rates of NH_4NO_3 in the "Various Forms of N Trial." NH_4NO_3 did not increase soluble Ca over the Check at depths below 12 cm in this experiment (Table 8).

Extractable Ca:Na ratio. Within the Ap horizon, applications of NH_4NO_3 resulted in the selective leaching of Na as compared to Ca. This is reflected in an extractable Ca:Na ratio of 2.75 vs. 3.38 for the Check. A slight increase in Ca coupled with a significant loss of Na also resulted in a noticeable improvement of the Ca:Na ratio within the upper Bnt (Table 7). Results such as these agree with the literature with respect to selective desorption (Ryzhova and Gorbunov, 1975; Poonia and Talibudeen, 1977) and leaching (van Schaik and Cairns, 1969) of Na vs. Ca. Differences for the Ca:Na ratio in the lower Bnt are negligible. An interesting trend is noted in the portion of the Csk sampled. That is, Na is slightly increased in the NH_4NO_3 treatment, possibly as an accumulation from leaching of the upper horizons, while Ca remains constant in this zone. The net result is a lower Ca:Na ratio for NH_4NO_3 as compared to the Check. A significant correlation between Na and Ca is recorded in the Ap horizon ($p \leq 0.01$) and the upper Bnt ($p \leq 0.05$), although the latter coefficient is negative and of less magnitude (Table 9).

Soil Mg. Extractable and soluble Mg were significantly decreased by NH_4NO_3 in the Ap ($p \leq 0.01$) and upper Bnt horizons

($p \leq 0.05$). Below this depth, no differences for extractable Mg resulted from the application of N fertilizer (Table 7). There is a difference ($p \leq 0.05$) between values for soluble Mg in the Csk horizon (Table 8). Mg can favorably influence the stabilization of soil colloids (van Schaik and Cairns, 1969) and is required by plants as a nutrient (Doll and Lucas, 1973). High losses of Mg as occurred in the Ap and upper Bnt horizons, then, must be of some concern. Extractable Mg is highly correlated with pH, Na, and Ca within the Ap horizon, as well as Na in the upper Bnt ($p \leq 0.01$, Table 9).

Summary of soil analyses. Yearly applications of NH_4NO_3 over 12 years at a rate of 300 kg/ha N per year significantly depressed extractable Na, Ca, Mg, K and pH within the Ap horizon of a Duagh SiL while causing marked increases of extractable Al, Mn and exchange acidity within the same horizon. In addition, NH_4NO_3 influenced several soil parameters to greater depths within the soil profile. Extractable Na, Mg, K and exchange acidity were affected into the upper Bnt, to a depth of 17 cm. Extractable K was significantly decreased and exchange acidity increased consistently throughout the Ap and Bnt horizons. The data, then, show that real differences occurred from high application rates of NH_4NO_3 . It is also noteworthy that all of the effects were most dramatic in the surface horizon which indicates they are resultant of surface applications of NH_4NO_3 ; and the degree to which these effects are manifest decreases with depth. Correlation coefficients show the same pattern with virtually all soil parameters significantly related in the Ap horizon ($p \leq 0.01$).

Table 7. Soil analyses for a Duagh SiL receiving long-term applications of a high rate of NH₄NO₃ vs Check

Treatment	Rate N kg/ha	Horizon	Depth cm	CEC meq/100 g	pH 1:2½	Ca:Na [†]	Extractable Cations						
							meq/100 g					ppm	
							Na	Ca	Mg	K	H ⁺	Al	Mn
NH ₄ NO ₃	300			36.75	4.66 **	8.75	1.18 **	10.32 **	1.99 **	1.06 **	20.36 **	13.27 **	56.15 **
Check	0	Ap	0-12	38.26	6.20	3.38	4.96	16.75	6.22	1.41	12.14	5.14	23.54
NH ₄ NO ₃	300			37.78	7.05 **	2.52	7.57 **	19.08	7.14 *	0.54 **	5.52 **	3.74	11.87
Check	0	Bnt	12-17	35.64	7.62	1.38	11.85	16.38	11.47	0.91	3.86	3.45	12.51
NH ₄ NO ₃	300			40.96	8.03	1.32	13.80	18.16	13.92	0.68 **	2.87 **	3.35 *	6.24
Check	0	Bnt	17-27	42.45	8.00	1.19	14.27	17.02	12.84	0.84	1.88	1.72	6.98
NH ₄ NO ₃	300			35.01	8.18	1.19	19.33	23.07	13.64	0.62	0.21	2.60	9.71
Check	0	Csk	27-37	34.29	8.25	1.55	15.42	23.97	12.86	0.70	0.02	2.19	8.89

[†] Ca:Na ratio data was not t tested for statistical differences

⁺ H⁺ Exchange acidity

** T tested significant differences $p \leq 0.01$

* T tested significant differences $p \leq 0.05$

Table 8. Soil analyses for a Duagh SiL receiving long-term repeated applications of NH_4NO_3 vs Check; soluble cations

Treatment	Yearly Rate N kg/ha	Horizon	Depth cm	EC mmhos/cm	Soluble Cations				
					meq/100 g			ppm	
					Na	Ca	Mg	K	Mn
NH_4NO_3	300			0.50	0.71 **	1.06 **	0.53 **	0.13	8.98 **
Check	0	Ap	0-12	0.42	1.68	0.46	0.30	0.11	3.80
NH_4NO_3	300			0.50	2.22 **	0.76	0.64 *	0.07 **	1.08 *
Check	0	Bnt	12-17	0.61	2.75	1.12	1.48	0.15	2.30
NH_4NO_3	300			0.72	3.09	1.14	1.14	0.11	1.33
Check	0	Bnt	17-27	0.88	3.53	1.16	1.40	0.17	2.02
NH_4NO_3	300			2.72	12.61	2.99	4.16 *	0.20	0.78
Check	0	Csk	27-37	2.40	12.04	1.88	5.99	0.22	0.84

** T tested significant differences $p \leq 0.01$

* T tested significant differences $p \leq 0.05$

Table 9. Correlation of pH and extractable cations for Check vs. NH_4NO_3 applied at 300 kg/ha N annually for 12 years on a Duagh Sil

Soil Horizon	Depth cm	Extractable									
		pH	Na	Ca	Mg	K	Al				Mn
Ap	0-12	Na	0.92**	--							
		Ca	0.86**	0.79**	--						
		Mg	0.92**	0.92**	0.81**	--					
		K	0.81**	0.72**	0.36	0.81**	--				
		Al	-0.94**	-0.85**	-0.77**	-0.92**	-0.87**	--			
		Mn	-0.92**	-0.84**	-0.76**	-0.83**	-0.71**	0.87**	--		
Bnt	12-17	Na	0.57**	--							
		Ca	-0.47*	-0.51*	--						
		Mg	0.34	0.57**	-0.14	--					
		K	0.63**	0.58**	-0.02	0.64**	--				
		Al	0.01	-0.05	-0.12	-0.37	-0.07	--			
		Mn	0.37	-0.21	0.09	0.02	-0.19	0.11	--		

Table 9. (continued)

Soil Horizon	Depth cm	pH	Extractable						
			Na	Ca	Mg	K	Al	Mn	
Bnt	17-27	Na	--						
		Ca	-0.38	--					
		Mg	-0.36	0.08	--				
		K	-0.17	0.18	-0.51*	--			
		Al	-0.25	-0.17	0.35	-0.11	--		
		Mn	0.06	0.16	0.10	0.30	-0.46*	--	
Csk	27-37	Na	--						
		Ca	0.31	--					
		Mg	-0.03	-0.41	--				
		K	-0.12	0.41	-0.34	--			
		Al	0.10	0.06	0.22	-0.01	--		
		Mn	0.27	0.26	0.07	0.22	0.22	--	

** Correlations significant at $p \leq 0.01$.

* Correlations significant at $p \leq 0.05$. (20 pairs of data)

Furthermore, as treatment effects become lessened with depth, so do the correlation coefficients, and no significant correlations ($p \leq 0.01$) exist below a depth of 17 cm (Table 9).

Greenhouse Data

Introduction. Soils from the Ap horizons of the Check and $(\text{NH}_4)_2\text{SO}_4$ treatment of the "Various Forms of N Trial" were utilized in the greenhouse study. Laboratory analyses had shown that the effects of $(\text{NH}_4)_2\text{SO}_4$ were more pronounced than for the other N fertilizer treatments in the "Various Forms of N Trial." In the greenhouse, both Check and $(\text{NH}_4)_2\text{SO}_4$ treated field soils each received the same amendments (Table 1). The chemical amendments were added to alter the N, Ca and pH status of the Check field soil and the $(\text{NH}_4)_2\text{SO}_4$ field treated soil. The greenhouse trial was designed to evaluate the effect that each of these parameters had on yield and chemical composition of barley plants grown on the two field soils selected. The greenhouse Control denotes both Check and $(\text{NH}_4)_2\text{SO}_4$ treated field soils, that each received K and P in the form of KH_2PO_4 , but to which no additions of N or Ca were made in the greenhouse.

Data for soil pH before and after the greenhouse experiment, as well as total dry matter yield and chemical composition of barley plants are recorded in Table 10. Significant differences are calculated at $p \leq 0.01$. The same analysis data, with significant differences recorded at $p \leq 0.05$ are found in Appendix C.

Soil pH. The Ap horizon that received $(\text{NH}_4)_2\text{SO}_4$ applications in the field had a significantly lower pH than the field Check before cropping in the greenhouse ($p \leq 0.01$). At the termination of the greenhouse study, all treatments on $(\text{NH}_4)_2\text{SO}_4$ field soil had lower pH values than the corresponding treatments applied to the Check field soil ($p \leq 0.01$) except in the case of CaCO_3 additions (Table 10). CaCO_3 was added in sufficient quantities to adjust soil pH to approximately 6.5. The soil receiving $(\text{NH}_4)_2\text{SO}_4$ in the field required nearly four times the rate of CaCO_3 as compared to the Check field soil to adjust both to a pH near 6.5.

Additions of $(\text{NH}_4)_2\text{SO}_4$ in the greenhouse significantly decreased the pH of the Check field soil relative to the greenhouse Control for the same soil; but greenhouse applications of $(\text{NH}_4)_2\text{SO}_4$ compared to the Control on the $(\text{NH}_4)_2\text{SO}_4$ field soil did not significantly depress soil pH (Table 10). In addition, although $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ significantly depressed pH over CaSO_4 alone on the Check field soil, the same significant differences did not occur in the $(\text{NH}_4)_2\text{SO}_4$ field soil (Table 10). The fact that additions of $(\text{NH}_4)_2\text{SO}_4$ in the greenhouse did not significantly lower the pH of the $(\text{NH}_4)_2\text{SO}_4$ field soil while the $(\text{NH}_4)_2\text{SO}_4$ greenhouse treatments markedly lowered pH ($p \leq 0.01$) on the Check field soil leads to speculation that nitrification and resultant acidification may have been retarded by the acidic nature of the $(\text{NH}_4)_2\text{SO}_4$ field soil. Earlier, Cairns (1972b) found that increasing the pH of the Ap of a Duagh SiL improved N utilization. As compared to the greenhouse Control, CaSO_4 and

$\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ each significantly lowered the pH within the field Check and $(\text{NH}_4)_2\text{SO}_4$ field soils ($p \leq 0.01$). $\text{Ca}(\text{NO}_3)_2$ did not alter the pH of either field soil.

Dry matter yield of barley. There are several significant differences in barley yields among treatments considered, and also interactions worthy of note. Within the Check field soil, none of the greenhouse treatments significantly lowered yields as compared to the Control. On the other hand, applications of $(\text{NH}_4)_2\text{SO}_4$, CaSO_4 and $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ each significantly depressed yields on the $(\text{NH}_4)_2\text{SO}_4$ field soil ($p \leq 0.01$; Table 10). The importance of soil pH as it affects yields on the $(\text{NH}_4)_2\text{SO}_4$ field soil is emphasized by the observation that the adjustment of pH to near 6.5 results in improved dry matter yields as compared to the Control, and all other greenhouse treatments that depressed pH on this particular field soil (Table 10). Soil pH and yields are significantly ($p \leq 0.01$) correlated (Table 11).

Several observations elucidate the specific role of soil pH as it affected yields in the greenhouse trial. Several significant effects of pH on the yield within the $(\text{NH}_4)_2\text{SO}_4$ field soil are not reflected in the Check field soil. Greenhouse treatments of $\text{Ca}(\text{NO}_3)_2$ and $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ both supplied the same amounts of Ca and N. $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$, as compared to $\text{Ca}(\text{NO}_3)_2$, significantly depressed soil pH on both field soils ($p \leq 0.01$; Table 10). The depression of pH caused by $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ vs. $\text{Ca}(\text{NO}_3)_2$ corresponds to less

vigorous barley growth in the $(\text{NH}_4)_2\text{SO}_4$ field soil, but this same effect is not noticed on the Check field soil (Table 10; Plate 1). In addition, the significantly higher soil acidity ($p \leq 0.01$) in the CaSO_4 treatments as compared to CaCO_3 did not effectively decrease barley vigor in the Check field soil, but growth reduction is clearly evident for the $(\text{NH}_4)_2\text{SO}_4$ field soil (Table 10; Plate 2). Therefore, it seems that although a change of pH induced by additions of salts can be important in affecting yield results, perhaps more significant is the actual pH value at which the soil stabilizes. Generally, fluctuations of pH in the range of 5.6 to 6.5 did not affect yield as drastically as fluctuations of pH 4.6 - 4.9. This suggests that reduction of soil pH below certain threshold levels for this soil can cause significant yield losses as continued subtle decreases of pH occur. This is closely linked to the concept that toxic quantities of Al and Mn may rapidly increase in availability below specific pH levels.

$\text{Ca}(\text{NO}_3)_2$ was most effective in stimulating maximum yield responses on both Check and $(\text{NH}_4)_2\text{SO}_4$ field soils (Table 10). While supplying the same amount of N as $(\text{NH}_4)_2\text{SO}_4$, $\text{Ca}(\text{NO}_3)_2$ resulted in significantly higher yields ($p \leq 0.01$) for $\text{Ca}(\text{NO}_3)_2$ vs. $(\text{NH}_4)_2\text{SO}_4$ on both field soils (Table 10; Plate 3). In addition, $\text{Ca}(\text{NO}_3)_2$ seems to have a special ability to raise barley yield in the $(\text{NH}_4)_2\text{SO}_4$ field soil, and yields at pH 4.9 for this soil paralleled those of $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ treatments on the Check soils which had pH 5.6 and 5.7, respectively (Table 10). This suggests that

perhaps readily available Ca from $\text{Ca}(\text{NO}_3)_2$ may have an ability to positively influence the yield of the acidified $(\text{NH}_4)_2\text{SO}_4$ field soil. However, additions of CaCO_3 and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ potentially supplied much more Ca and resulted in significantly higher uptake of Ca on the $(\text{NH}_4)_2\text{SO}_4$ field soil as compared to $\text{Ca}(\text{NO}_3)_2$; yet these treatments did not increase yields over $\text{Ca}(\text{NO}_3)_2$ (Table 10). Additions of $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ had no effect in increasing plant vigor compared to $\text{Ca}(\text{NO}_3)_2$ on the Check field soil, while crop response was markedly poorer for $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ on the $(\text{NH}_4)_2\text{SO}_4$ field soil (Plate 4). Yield data reflect the same pattern. Yields are significantly lower for $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ as compared to $\text{Ca}(\text{NO}_3)_2$ on the $(\text{NH}_4)_2\text{SO}_4$ field soil although pH and Ca uptake are significantly higher for the $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ treatment ($p \leq 0.01$; Table 10). A possible explanation for the foregoing observation is that Ca and CO_3 from the CaCO_3 were probably not readily available at time of germination; but rather became dissociated over the span of the trial and ultimately raised pH. The treatments were not incubated in the soil prior to seeding and commencement of the greenhouse study. Therefore, barley seedlings in the $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ treatment on the $(\text{NH}_4)_2\text{SO}_4$ field soil may have been severely hampered by low pH and its ramifications within initial stages of the experiment. With time, however, the pH would be expected to rise. A soil pH of 6.4 was recorded for this treatment at the termination of the greenhouse trial.

Generally, the additions of N in the form of $(\text{NH}_4)_2\text{SO}_4$ did not stimulate barley growth (Table 10). In the case of the acidified

$(\text{NH}_4)_2\text{SO}_4$ field soil, greenhouse additions of $(\text{NH}_4)_2\text{SO}_4$ significantly decreased yields and soil pH as compared to the Control receiving no N treatment ($p \leq 0.01$; Table 10).

Barley uptake of Al. Soil pH appears to have a direct effect on the Al composition of barley, although the treatments that depressed soil pH most severely did not necessarily cause the highest levels of plant Al (Table 10). It is of salient interest that the lowest yield in the trial was recorded for $(\text{NH}_4)_2\text{SO}_4$ in the acidified field soil and that this treatment also resulted in the highest concentration of Al in plant tissue (Table 10). Also, the lowest values of plant Al, though not significantly so in all cases, corresponded to the highest yields on the $(\text{NH}_4)_2\text{SO}_4$ field soil. Little variation of Al content of barley plants among treatments is recorded for the Check field soil and the lowest values, though not significantly different ($p \leq 0.01$) from the other treatments on the same field soil are recorded for CaCO_3 and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$. These treatments also correspond to the highest pH values for the Check field soil (Table 10). Significant negative correlations for both soil pH and yield each exist with plant Al ($p \leq 0.01$; Table 11). $\text{Ca}(\text{NO}_3)_2$, though it did not significantly raise pH, was as effective as CaCO_3 and more effective than $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ in reducing the Al content of barley plants grown on the $(\text{NH}_4)_2\text{SO}_4$ field soil, although differences were not significant ($p \leq 0.01$).

Barley uptake of Mn. Soil pH and barley yield are each very strongly correlated to plant Mn. Correlations for pH and yield are more closely related to plant analysis data for Mn than they are with Al (Table 11). Plant uptake of Mn is also significantly correlated with plant Al ($p \leq 0.01$). CaCO_3 and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ which both significantly increased pH dramatically reduced the Mn content of barley compared to all other treatments on the $(\text{NH}_4)_2\text{SO}_4$ field soil (Table 10.). As well, all greenhouse treatments on the $(\text{NH}_4)_2\text{SO}_4$ field soil, except for CaCO_3 and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$, corresponded to a significantly lower soil pH than treatments on the Check field soil. These consequently resulted in significantly higher concentrations of plant Mn which were several times the levels encountered for greenhouse treatments on the Check field soil. The plant uptake data reflect that extractable Mn was significantly higher for the Ap horizon of the acidified $(\text{NH}_4)_2\text{SO}_4$ field soil than for the Check field soil ($p \leq 0.05$; Table 3).

Barley uptake of Na. Plant analysis data reveal that significantly lower concentrations of Na are found in plants grown on the Ap horizon of the $(\text{NH}_4)_2\text{SO}_4$ field soil as compared to the Check field soil ($p \leq 0.01$). Soil analysis showed lesser amounts of Na in the Ap horizon of the $(\text{NH}_4)_2\text{SO}_4$ treatments in the field as compared to the Check soil (Table 6), and plant uptake is probably a function of the amounts of Na present in the original field soils. CaCO_3 , $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$ seemed to stimulate Na uptake within the Check field soil (Table 10). There is a significant

($p \leq 0.05$) correlation between plant uptake of Na and soil pH (Table 11).

Barley uptake of Ca. Generally, treatments on the Check field soil resulted in slightly higher Ca uptake than equivalent treatments on the $(\text{NH}_4)_2\text{SO}_4$ field soil, although differences are not universally significant ($p \leq 0.01$; Table 10). The exceptions are the Control, for which values of plant Ca were identical for both field soils, and CaCO_3 as well as $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ treatments on the $(\text{NH}_4)_2\text{SO}_4$ field soil. The latter two treatments each supplied 5,733 ppm Ca and resulted in significantly higher uptake of Ca than did other treatments ($p \leq 0.01$). Poonia and Bhumbra (1973) reported that additions of CaCO_3 significantly increased the Ca content of barley grown on an alkaline Na-affected soil, even though the salt did not readily dissociate. They concluded that the presence of Ca salt acted in supplying soluble Ca and also as a labile pool supplying Ca throughout the length of the greenhouse experiment. Additions of CaSO_4 did not significantly raise Ca uptake over the Control in both field soils, while $\text{Ca}(\text{NO}_3)_2$ did ($p \leq 0.01$). Harker et al. (1977) reported that supplying N, P and K to a Duagh SiL led to increased Ca uptake by barley in the greenhouse. However, additions of $(\text{NH}_4)_2\text{SO}_4$ to both $(\text{NH}_4)_2\text{SO}_4$ and Check field soils did not significantly raise the Ca content of barley in the experiment currently under discussion (Table 10). Ca content of barley was not significantly correlated to yield (Table 11), indicating factors other than Ca nutrition, namely acidity, probably have a more profound influence on yields.

Ca:Na ratio within barley tissue. The Ca:Na ratios of barley plants for the $(\text{NH}_4)_2\text{SO}_4$ field soil are somewhat higher than ratios for the Check field soil, except in the case of CaCO_3 and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ treatments. The higher plant Ca:Na ratios for the $(\text{NH}_4)_2\text{SO}_4$ field soil is somewhat surprising in view of the fact that soil Ca:Na ratios were slightly lower to approximately equal for the $(\text{NH}_4)_2\text{SO}_4$ treated Ap vs. the Check Ap horizon (Table 6). CaCO_3 and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ applied on the $(\text{NH}_4)_2\text{SO}_4$ field soil resulted in the highest Ca:Na ratios and reflect higher uptake of Ca due to the large amounts of CaCO_3 added to adjust soil pH.

Barley uptake of Mg. All values for plant Mg are significantly lower ($p \leq 0.01$) on the $(\text{NH}_4)_2\text{SO}_4$ field soil as compared to the Check field soil (Table 10). Extractable Mg in the Ap horizon of Duagh SiL was markedly depressed by additions of $(\text{NH}_4)_2\text{SO}_4$ in the field and levels of Mg in the plants appear to directly reflect the soil status. Mg content of plant tissue is correlated ($p \leq 0.01$) to each of soil pH, yield, and plant Na. Negative correlations of lesser magnitude, but significant ($p \leq 0.01$), exist between Mg and Al as well as Mg and Mn (Table 11).

Barley uptake of K. Overall, there are few significant shifts in the level of plant K. Generally, K is higher, though not significantly so ($p \leq 0.01$) for $(\text{NH}_4)_2\text{SO}_4$ field soils vs. Check (Table 10). In the field, applications of $(\text{NH}_4)_2\text{SO}_4$ had a tendency to raise extractable soil K as compared to the Check (Table 6).

Within the greenhouse experiment, treatments made to the $(\text{NH}_4)_2\text{SO}_4$ field soil that depressed pH had some effect on increasing the K content of barley, although only $(\text{NH}_4)_2\text{SO}_4$ and $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ significantly increased plant K vs. the Control ($p \leq 0.01$; Table 10). A significant, negative correlation ($p \leq 0.05$) exists for plant K and barley yield, while significant correlations occur for plant K and each of Al and Mn (Table 11).

Summary of results from the greenhouse trial. In the greenhouse, total dry matter yields of barley grown on the Ap horizon of a Duagh SiL that had previously received repeated long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field, were depressed relative to yields obtained from a Check Ap that had received no N fertilizer in the field. $(\text{NH}_4)_2\text{SO}_4$ had been added over a 10-year period in the field at an annual rate of 112 kg/ha N. Soil analysis indicated a pH, before cropping in the greenhouse, of 4.75 for the $(\text{NH}_4)_2\text{SO}_4$ field soil as compared to 5.88 for the Check field soil. Greenhouse treatments on the $(\text{NH}_4)_2\text{SO}_4$ (acidified) field soil that contributed to further decreases in pH caused additional losses in yields. Analysis of plant material indicated undesirable levels of Al and Mn were present in barley grown on treatments corresponding to decreased soil pH and low productivity. Additions of CaCO_3 alone and in combination with $(\text{NH}_4)_2\text{SO}_4$ increased soil pH to approximately 6.5 and resulted in dramatically decreased levels of Al and Mn in plant tissue grown on these treatments. CaCO_3 and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ distinctly improved

the productivity of the $(\text{NH}_4)_2\text{SO}_4$ field soil. These observations indicate that a major problem does exist within the Ap horizon of the $(\text{NH}_4)_2\text{SO}_4$ field soil, and that it is directly related to acidity and toxic quantities of available Al and Mn within the soil system.

$\text{Ca}(\text{NO}_3)_2$ treatments were especially effective in stimulating increased yields, particularly on the $(\text{NH}_4)_2\text{SO}_4$ field soil even though $\text{Ca}(\text{NO}_3)_2$ did not increase soil pH. This leads to some speculation that readily available Ca may suppress some of the symptoms of low soil pH encountered in the Ap horizon of the $(\text{NH}_4)_2\text{SO}_4$ field soil. An overview of the greenhouse experiment indicates that Ca and N had their greatest effect on improving productivity when they were applied in combination.

Yields of brome grass in the field over a period of 10 years had shown positive response to the applications of $(\text{NH}_4)_2\text{SO}_4$, even though the treatment had altered chemical properties and effectively acidified the surface horizon. Elliott et al. (1973) identified a relatively high species tolerance of brome grass to soil acidity and concomitant high levels of Al and Mn. As well, the brome grass stand in the field was well established and had developed a root mass into the Bnt horizon, where soil acidity and related problems had not developed. In the greenhouse, however, the growth of barley seedlings was seriously hampered by the acidic environment of the Ap horizon developed under repeated applications of $(\text{NH}_4)_2\text{SO}_4$.

Table 10. Soil pH after cropping, dry matter and chemical composition of barley plants grown on the Ap horizon of a Duagh SiL Check and a Duagh Ap that received long-term treatments of $(\text{NH}_4)_2\text{SO}_4$ at a rate of 112 kg/ha N per year in the field prior to greenhouse experiment

Field Soil	Greenhouse Treatment	1:2½ pH	g Total Dry Matter	%					ppm		
				Na	Ca	Mg	K	Al	Mn	Ca:Na ⁺	
Check	Control	6.02 ^g	3.17 ^{cde}	0.73 ^b	0.61 ^{ab}	0.46 ^{cd}	3.48 ^a	74.8 ^a	151.5 ^c	0.84	
	$(\text{NH}_4)_2\text{SO}_4$	5.68 ^{de}	3.18 ^{cde}	0.84 ^{bc}	0.70 ^{bcd}	0.51 ^{de}	3.70 ^{abc}	83.5 ^{ab}	123.2 ^{abc}	0.83	
	$\text{Ca}(\text{NO}_3)_2$	6.05 ^g	4.01 ^g	0.92 ^{cd}	0.84 ^{ef}	0.58 ^f	3.60 ^{ab}	82.8 ^{ab}	73.5 ^{ab}	0.91	
	CaSO_4	5.74 ^{ef}	3.38 ^{def}	0.74 ^b	0.74 ^{bcde}	0.54 ^{ef}	3.95 ^{abc}	94.5 ^{abc}	173.2 ^c	1.00	
Duagh Ap	$\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$	5.56 ^d	3.55 ^{efg}	0.82 ^{bc}	0.71 ^{bcd}	0.54 ^{ef}	3.77 ^{abc}	89.5 ^{ab}	117.2 ^{abc}	0.87	
	CaCO_3	6.50 ^{hi}	2.81 ^c	1.04 ^d	0.80 ^{def}	0.52 ^e	3.76 ^{abc}	76.8 ^a	63.8 ^{ab}	0.77	
	$\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$	6.18 ^g	3.72 ^{fg}	0.99 ^d	0.89 ^f	0.52 ^e	3.92 ^{abc}	71.2 ^a	56.2 ^a	0.90	
Before cropping		5.88 ^f	---	---	---	---	---	---	---	---	

Table 10. (continued)

Field Soil	Greenhouse Treatment	1:2½ pH	g Total Dry Matter	%				ppm			Ca:Na ⁺
				Na	Ca	Mg	K	Al	Mn		
(NH ₄) ₂ SO ₄	Control	4.92 ^c	2.01 ^b	0.52 ^a	0.61 ^{ab}	0.34 ^a	3.58 ^{ab}	119.8 ^{bc}	671.5 ^d	1.17	
	(NH ₄) ₂ SO ₄	4.79 ^{bc}	1.39 ^a	0.56 ^a	0.55 ^a	0.38 ^{ab}	4.47 ^d	127.5 ^c	927.5 ^{ef}	0.98	
	Ca(NO ₃) ₂	4.92 ^c	3.38 ^{def}	0.57 ^a	0.76 ^{cde}	0.42 ^{bc}	3.91 ^{abc}	88.5 ^{ab}	893.2 ^e	1.33	
	CaSO ₄	4.68 ^{ab}	1.48 ^a	0.49 ^a	0.65 ^{abc}	0.40 ^b	4.09 ^{bcd}	96.0 ^{abc}	957.8 ^{ef}	1.33	
	CaSO ₄ + (NH ₄) ₂ SO ₄	4.60 ^a	1.48 ^a	0.49 ^a	0.63 ^{abc}	0.37 ^{ab}	4.14 ^{cd}	106.5 ^{abc}	963.2 ^f	1.29	
	CaCO ₃	6.55 ⁱ	2.96 ^{cd}	0.52 ^a	1.06 ^g	0.42 ^{bc}	3.86 ^{abc}	88.5 ^{ab}	144.2 ^c	2.04	
	CaCO ₃ + (NH ₄) ₂ SO ₄	6.39 ^h	2.80 ^c	0.49 ^a	1.07 ^g	0.40 ^b	4.09 ^{bcd}	96.8 ^{abc}	132.2 ^{bc}	2.18	
	Before cropping	4.75 ^{ab}	---	---	---	---	---	---	---	---	

Values within each column and followed by differing letters are significantly different ($p \leq 0.01$).

+ Ratio of plant uptake Ca:Na. Ca:Na ratio data was not subjected to Duncan's new multiple range test for significant differences.

Table 11. Correlation of soil pH after cropping, yield and chemical composition data of barley plants grown in the greenhouse on the Ap horizon of a Duagh SiL Check and a Duagh Ap receiving long-term treatments of $(\text{NH}_4)_2\text{SO}_4$ at a rate of 112 kg/ha N per year

	Soil pH	Plant analysis data						
		Yield	Na	Ca	Mg	K	Al	Mn
Soil pH	--							
Yield	0.66**	--						
Na	0.54*	0.66**	--					
Ca	0.76**	0.47	0.10	--				
Mg	0.55*	0.81**	0.87**	0.22	--			
K	-0.41	-0.59*	-0.46	-0.04	-0.43	--		
Al	-0.74**	-0.75**	-0.68**	-0.43	-0.70**	0.55*	--	
Mn	-0.92**	-0.78**	-0.69**	-0.44	-0.74**	0.56*	0.68**	--

** Correlations significant at $p \leq 0.01$.

* Correlations significant at $p \leq 0.05$.

(14 pairs of data)

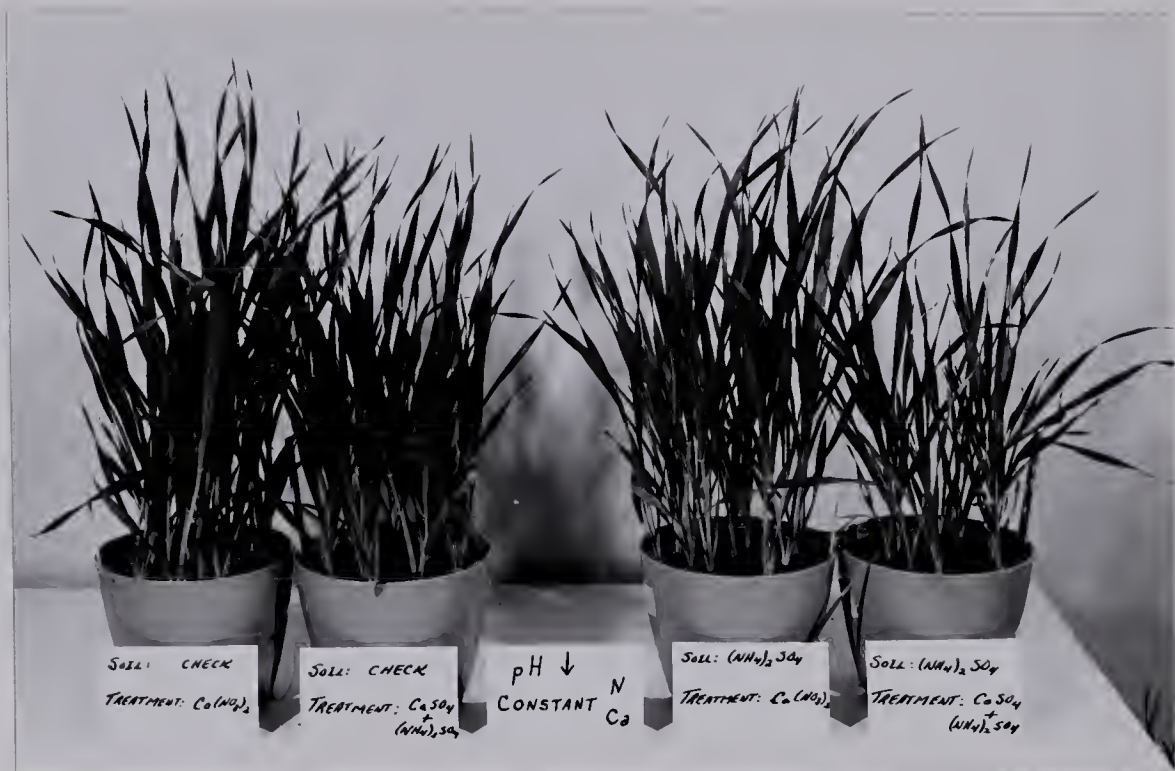


Plate 1. The effect of greenhouse applications of $\text{Ca}(\text{NO}_3)_2$ and $\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$ on production of barley grown on the Ap horizon of a Duagh SiL Check soil and the Ap horizon of Duagh SiL that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field.



Plate 2. The effect of greenhouse applications of CaCO_3 and CaSO_4 on production of barley grown on the Ap horizon of a Duagh SiL Check soil and the Ap horizon of Duagh SiL that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field.

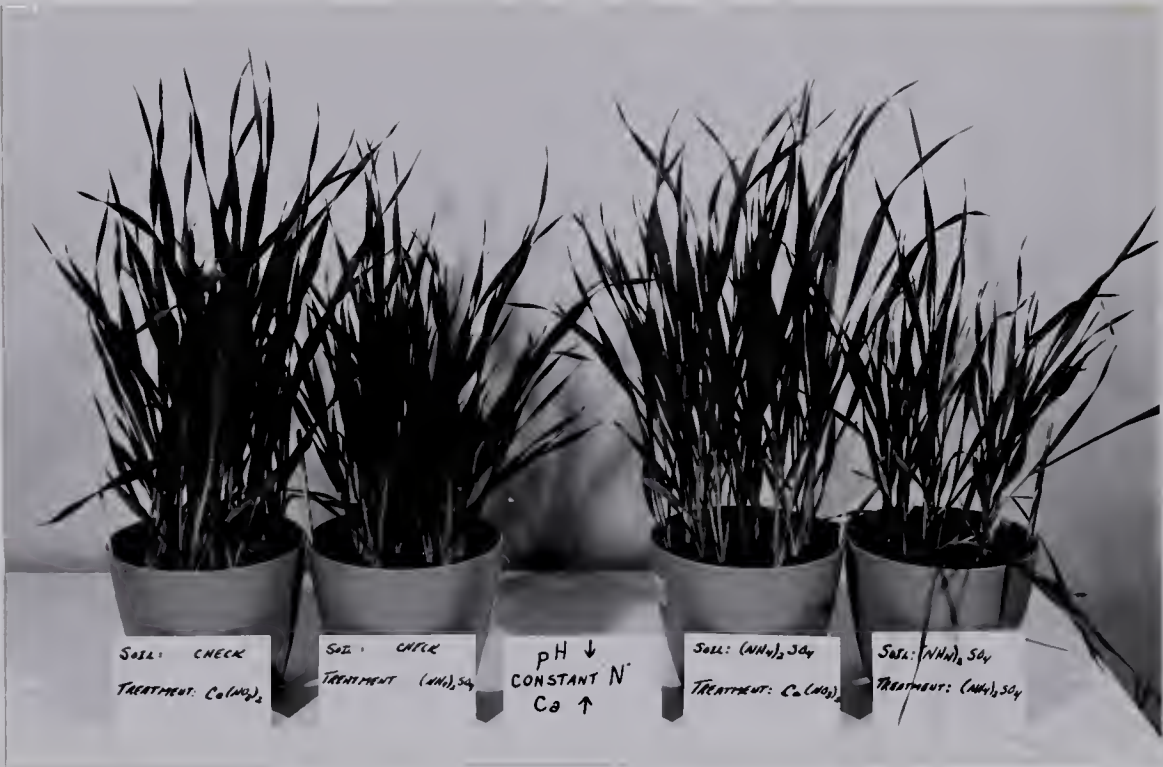


Plate 3. The effect of greenhouse applications of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ on production of barley grown on the Ap horizon of a Duagh SiL Check soil and the Ap of a Duagh SiL that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field.

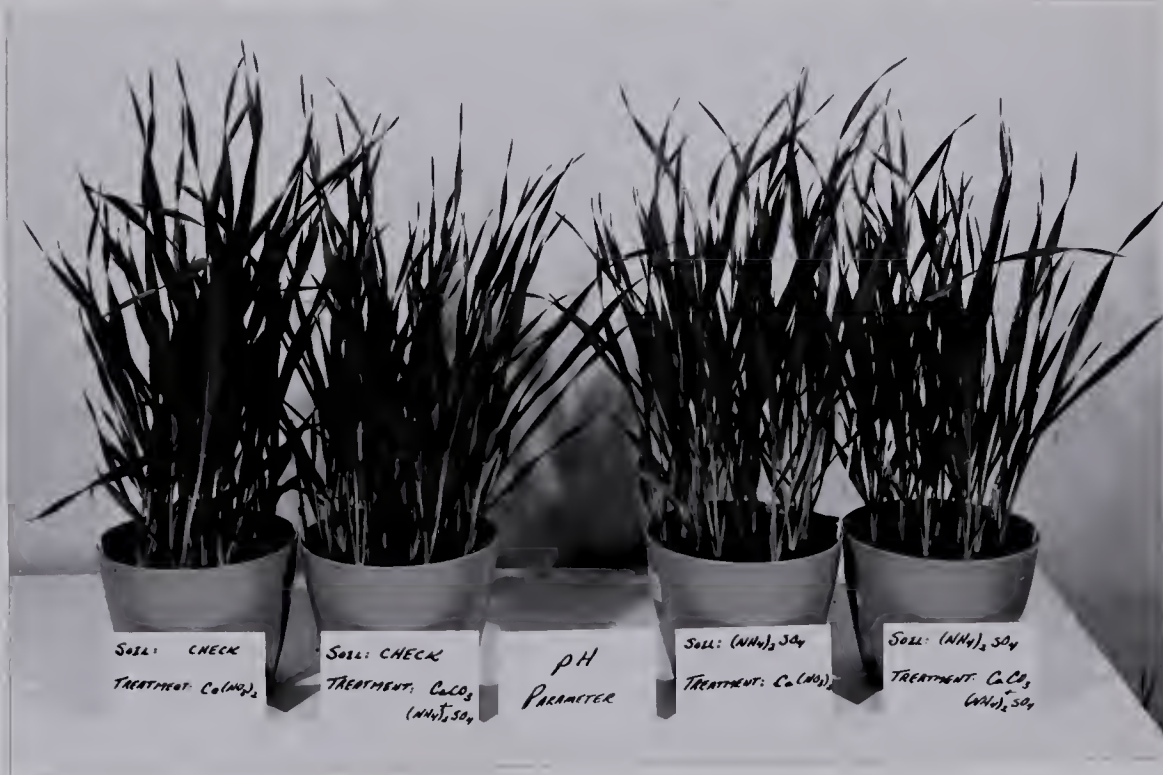


Plate 4. The effect of greenhouse applications of $\text{Ca}(\text{NO}_3)_2$ and $\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$ on production of barley grown on the Ap horizon of a Duagh SiL Check soil and the Ap of a Duagh SiL that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field.

GENERAL CONCLUSIONS

Soil analysis data clearly indicate that repeated applications of N fertilizers over a long period of time caused significant changes in the chemical properties of a Solonetzic soil. Soil samples studied were taken at several specific profile depths of a Duagh SiL which had received treatments of NH_4NO_3 , NH_2CONH_2 and $(\text{NH}_4)_2\text{SO}_4$ each applied at an annual rate of 112 kg/ha N. Applications of these amendments over a 10 year period had several profound effects on soil chemistry.

1. Each N fertilizer resulted in a net increase in the activity of H ions in the soil solution and also increased the exchange acidity of the soil. The degree of acidification was greatest for $(\text{NH}_4)_2\text{SO}_4$, followed by NH_4NO_3 , then NH_2CONH_2 and the acidification potential for each N source agreed with predictions based on the literature. NH_2CONH_2 caused only a slight increase in soil acidity as compared to results for an untreated Check.
2. The degree to which treatment effects were manifested decreased with depth, and generally even the most active treatments had little effect in the Bnt horizon. This is a clear indication that the effects are resultant of fertilizer applications made to the soil surface. $(\text{NH}_4)_2\text{SO}_4$ which caused the greatest degree of soil acidification, with few exceptions, affected chemical composition more dramatically and to greater depths than did other N treatments. NH_2CONH_2 generally affected soil chemistry very slightly and then usually only to shallow depths.

3. The pH values for the Ap horizon in the Check were near levels expected to yield toxicity symptoms due to soil acidity (Kamprath, 1970; Hoyt, 1977). Depression of pH by N fertilizer applications substantially raised NH_4OAc -extractable Al and Mn within the soil system.
4. Additions of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 increased the rate of leaching of Na, Ca and Mg within a Duagh SiL profile. The effects of $(\text{NH}_4)_2\text{SO}_4$ were more pronounced than were those for NH_4NO_3 and the former treatment decreased Na and Ca in the Ap and Bnt horizons, while Mg was affected only to the bottom of the Ap.
5. $(\text{NH}_4)_2\text{SO}_4$ caused a decrease of the extractable Ca:Na ratio in the Ap horizon. Within the Bnt, applications of $(\text{NH}_4)_2\text{SO}_4$ resulted in selective leaching of Na vs. Ca, and the extractable Ca:Na ratio was increased over the untreated Check. This is expected to improve the physical structure of the Bnt. NH_4NO_3 improved the extractable Ca:Na ratio in the Ap horizon, but few real differences occurred below this depth.
6. NH_2CONH_2 and NH_4NO_3 resulted in accelerated leaching of K in the Ap and upper Bnt horizons. $(\text{NH}_4)_2\text{SO}_4$ caused a net increase of soil K to the bottom of the Ap and it is evident that increased soil acidity due to application of the N fertilizer led to the release of K from soil minerals.

In another field experiment, the application of NH_4NO_3 at an annual rate of 300 kg/ha N over 12 years resulted in soil acidification and altered the chemical composition of Duagh SiL. Effects

of NH_4NO_3 were more noticeable in the upper regions of the soil profile and the majority of significant differences between the NH_4NO_3 treatment and the unfertilized Check were recorded within the Ap and upper portions of the Bnt horizons to a depth of 17 cm.

Applications of NH_4NO_3 altered chemical composition of a Duagh SiL in several ways.

1. A distinct decrease of soil pH from 6.2 to 4.7 occurred within the Ap horizon. A significant decrease in pH was also noted in the upper Bnt, although soil reaction remains near neutrality, and thus availability of Al and Mn was not affected. Exchange acidity was significantly increased by N fertilizer to the bottom of the Bnt (0-27 cm) although the actual and differential values of exchange acidity were rapidly reduced at depths below the Ap horizon.
2. In the Ap horizon concentrations of both extractable Al and Mn were more than doubled by applications of NH_4NO_3 . As soil pH increased in the Bnt horizon, levels of extractable Al and Mn dramatically decreased and differences between fertilizer treated and Check soils are non-existent for these ions.
3. NH_4NO_3 decreased Mg and Na within the Ap and upper Bnt horizons, while K was decreased into the lower levels of the Bnt horizon. The fact that pH was near neutrality in the upper Bnt and the low exchange acidity of this region leads to the conclusion that an overabundance of H ions was not present in the soil system. Therefore, NH_4 was probably responsible for the desorption and

subsequent leaching of K, Mg and Na within this portion of the soil profile.

4. Although there was a significant decrease of Ca in the Ap horizon under the influence of NH_4NO_3 , the relative loss of Na was greater resulting in a marked rise in the extractable Ca:Na ratio. A slight increase of Ca in the upper portion of the Bnt coupled with a major loss of Na resulted in a much improved Ca:Na ratio in this region. A slight improvement in the Ca:Na ratio of the lower Bnt horizon was also recorded.

The greenhouse experiment involved soils from the Check and $(\text{NH}_4)_2\text{SO}_4$ treated soils of the "Various Forms of N Trial" at Vegreville. The yield and chemical composition of barley grown on the Ap horizon of each field soil as affected by soil pH and additions of N and Ca were determined.

1. Plant uptake of Na, Mg, K, Al and Mn was a reflection of the soil levels for each particular element. Ca uptake was increased in most cases by additions of Ca salts in the greenhouse.
2. Soil pH had a most profound effect on productivity of barley. Yields of barley were generally depressed on the field soil acidified by $(\text{NH}_4)_2\text{SO}_4$ as compared to the Check field soil and were significantly correlated to soil pH.
3. The value for pH within the soil that had been acidified in the field by long-term application of $(\text{NH}_4)_2\text{SO}_4$ was in the region that is expected to cause toxic levels of Al and Mn within soil systems (Hoyt, 1977). Plant analyses show significantly higher levels of both elements in barley grown in the $(\text{NH}_4)_2\text{SO}_4$ field

soil vs. the Check field soil. Further depression of pH from greenhouse treatments on the field acidified soil caused additional increases of Al and Mn in barley and concomitantly depressed yield. Raising pH to 6.5 greatly improved productivity. These data led to the conclusion that the most significant cause of poor barley production on the Duagh Ap that had received long-term applications of $(\text{NH}_4)_2\text{SO}_4$ in the field was due to low pH and related Al and Mn toxicities within this soil. As well, toxic levels of Al and Mn became acute only below a certain pH level, and their effect increased with further depressions of pH. Fluctuations of pH above threshold levels had no influence on yield of barley grown on the Check field soil.

4. Barley yields on both field soils responded most dramatically to combined additions of Ca and N.

In summary, it is evident that repeated long-term applications of N fertilizers caused significant changes in the chemistry of a Duagh SiL soil. At a rate of 112 kg/ha N per year, $(\text{NH}_4)_2\text{SO}_4$ had more pronounced effects than did NH_4NO_3 or NH_2CONH_2 . In another nearby field experiment, NH_4NO_3 at 300 kg/ha N per year also significantly affected chemical characteristics of the Solonetzic soil. Both $(\text{NH}_4)_2\text{SO}_4$ at a moderate rate and the high rate of NH_4NO_3 resulted in improved extractable Ca:Na ratios within the Bnt horizon. The findings agree with predictions based on concepts of selective desorption of Ca vs. Na (Ryzhova and Gorbunov, 1975; Poonia and Talibudeen, 1977), and higher leaching rates for Na within the soil

profile (van Schaik and Cairns, 1969). The N fertilizers induced improvements in the Ca:Na ratio which are expected to increase water infiltration into the Duagh profile (Cairns and van Schaik, 1968), and thus act as ameliorative agents of the Solonetzic soil. However, the treatments that were most effective in improvement of the Ca:Na ratio also substantially increased the acidity of surface horizons. Under the influence of the effectively ameliorative N fertilizers, soil pH was reduced within the Ap horizon to levels expected to yield toxic concentrations of plant available Al and Mn. Though established brome grass responded positively to applications of N fertilizers on a Duagh SiL, barley grown on the Ap horizon in the greenhouse showed depressed yields due to decreased pH and related ion toxicities caused by long-term applications of $(\text{NH}_4)_2\text{SO}_4$. The results imply that if the sod were broken and seeded to cereals, severe productivity limitations would be expected as the seed would be placed and germinate within the acidified Ap horizon. As well, the removal of Ca and Mg from the surface horizon was enhanced by additions of N fertilizers, and loss of these nutrients is also a serious matter.

Soil productivity is a direct function of the ability of the soil system to provide an optimum environment for plant growth. Although the additions of N fertilizers improve the Ca:Na ratios, the resultant acidification can cause an overall loss of yield potential for certain crops. Adjusting the pH to 5.6 or higher and adding Ca to the treatments would have beneficial results. Additions of CaCO_3 in conjunction with N fertilizer treatments should maximize potential for overall amelioration of a Solonetzic soil.

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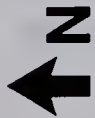
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Appendix A. Experimental field design: Various forms of N; Duagh SiL Vegreville, Alberta SE 1/4 17-52-14 W4

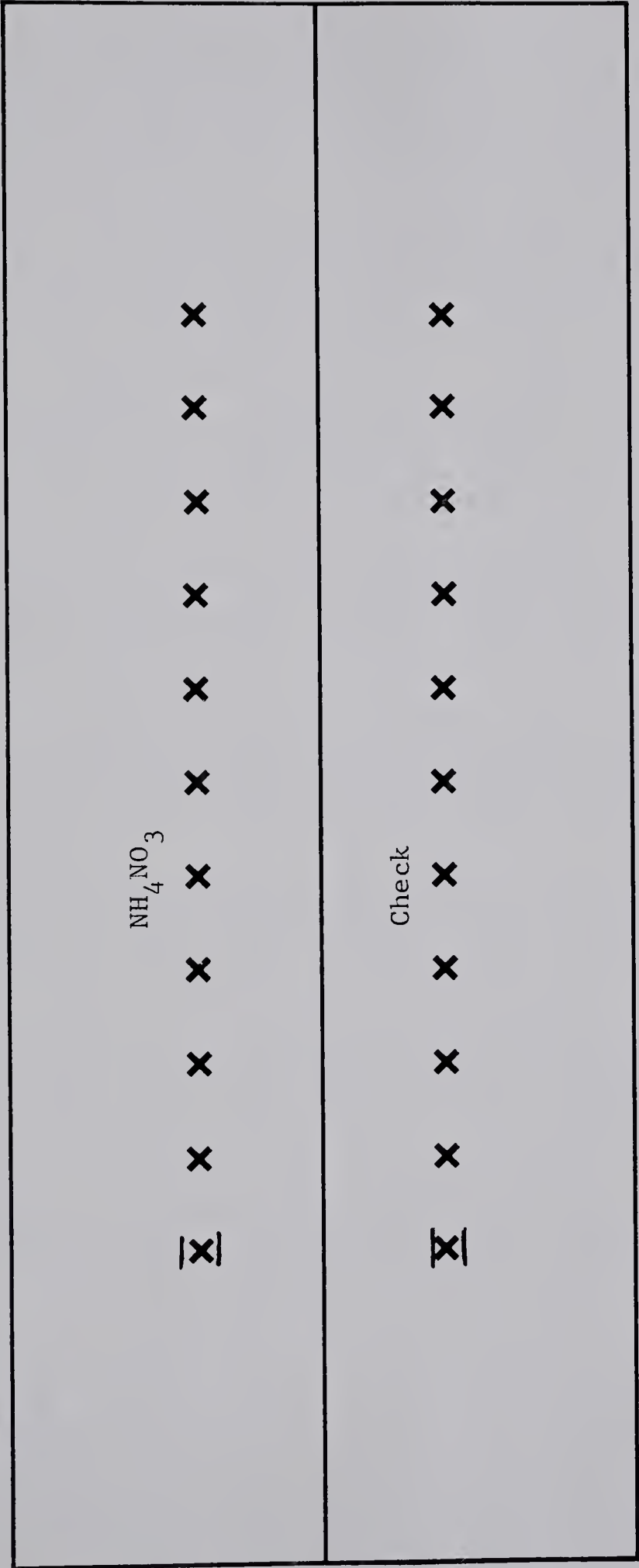
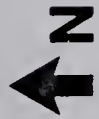


Trial dimensions:
6.0 x 9.0 m

2	3	4	
4	4	1	
3	1	2	
1	2	3	

	Rep. 1	Rep. 2	Rep. 3
Treatments	Annual Application Rates (kg/ha)		
	Total Fertilizer		
	Total N		
1. Check	0		0
2. NH ₄ NO ₃	335		112
3. NH ₂ CONH ₂	250		112
4. (NH ₄) ₂ SO ₄	535		112

Appendix B. Plot diagram: Fertility test; Duagh Sil
Vegreville, Alberta SE 1/4 17-52-14 W4



Treatments	Annual Application Rates (kg/ha)	
	Total Fertilizer	Total N
1. NH_4NO_3	897	300
2. Check	0	0

$\overline{\text{X}}$ denotes reference point.
 X denotes sampling sites.

Total dimensions: 6.0 x 15.0 m

Appendix C. Soil pH after cropping, dry matter and chemical composition of barley plants grown on the Ap horizon of a Duagh SiL Check and a Duagh Ap that received long-term treatments of $(\text{NH}_4)_2\text{SO}_4$ at a rate of 112 kg/ha N per year in the field prior to greenhouse experiment ($p \leq 0.05$)

Field Soil	Greenhouse Treatment	1:2½ pH	g Total Dry Matter	%					ppm		
				Na	Ca	Mg	K	Al	Mn	Ca:Na ⁺	
Check Duagh Ap	Control	6.02 ^g	3.17 ^{cd}	0.73 ^b	0.61 ^{ab}	0.46 ^d	3.48 ^a	74.8 ^a	151.5 ^{cd}	0.84	
	$(\text{NH}_4)_2\text{SO}_4$	5.68 ^e	3.18 ^{cd}	0.84 ^{bc}	0.70 ^{bcde}	0.51 ^e	3.70 ^{abc}	83.5 ^{ab}	123.2 ^{bcd}	0.83	
	$\text{Ca}(\text{NO}_3)_2$	6.05 ^g	4.01 ^f	0.92 ^{cd}	0.84 ^{gh}	0.58 ^f	3.60 ^{ab}	82.8 ^{ab}	73.5 ^{ab}	0.91	
	CaSO_4	5.74 ^e	3.38 ^{de}	0.74 ^b	0.74 ^{def}	0.54 ^e	3.95 ^{bcd}	94.5 ^{abc}	173.2 ^d	1.00	
	$\text{CaSO}_4 + (\text{NH}_4)_2\text{SO}_4$	5.56 ^d	3.55 ^{de}	0.82 ^{bc}	0.71 ^{cdef}	0.54 ^e	3.77 ^{abcd}	89.5 ^{ab}	117.2 ^{bc}	0.87	
	CaCO_3	6.50 ^j	2.81 ^c	1.04 ^d	0.80 ^{fgh}	0.52 ^e	3.76 ^{abcd}	76.8 ^a	63.8 ^a	0.77	
	$\text{CaCO}_3 + (\text{NH}_4)_2\text{SO}_4$	6.18 ^h	3.72 ^{ef}	0.99 ^d	0.89 ^h	0.52 ^e	3.92 ^{bcd}	71.2 ^a	56.2 ^a	0.90	
Before cropping		5.88 ^f	--	--	--	--	--	--	--	--	

Appendix C. (continued)

Field Soil	Greenhouse Treatment	1:2½ pH	g Total Dry Matter	%					ppm		
				Na	Ca	Mg	K	Al	Mn	Ca:Na ⁺	
(NH ₄) ₂ SO ₄	Control	4.92 ^c	2.01 ^b	0.52 ^a	0.61 ^{ab}	0.34 ^a	3.58 ^{ab}	119.8 ^{cd}	671.5 ^e	1.17	
	(NH ₄) ₂ SO ₄	4.79 ^b	1.39 ^a	0.56 ^a	0.55 ^a	0.38 ^b	4.47 ^e	127.5 ^d	927.5 ^{fg}	0.98	
	Ca(NO ₃) ₂	4.92 ^c	3.38 ^{de}	0.57 ^a	0.76 ^{efg}	0.42 ^c	3.91 ^{bcd}	88.5 ^{ab}	893.2 ^f	1.33	
	CaSO ₄	4.68 ^{ab}	1.48 ^a	0.49 ^a	0.65 ^{abcd}	0.40 ^{bc}	4.09 ^{cd}	96.0 ^{abc}	957.8 ^g	1.33	
	CaSO ₄ + (NH ₄) ₂ SO ₄	4.60 ^a	1.48 ^a	0.49 ^a	0.63 ^{abc}	0.37 ^{ab}	4.14 ^{de}	106.5 ^{bcd}	963.2 ^g	1.29	
	CaCO ₃	6.55 ^j	2.96 ^c	0.52 ^a	1.06 ⁱ	0.42 ^c	3.86 ^{abcd}	88.5 ^{ab}	144.2 ^{cd}	2.04	
	CaCO ₃ + (NH ₄) ₂ SO ₄	6.39 ⁱ	2.80 ^c	0.49 ^a	1.07 ⁱ	0.40 ^{bc}	4.09 ^{cd}	96.8 ^{abc}	132.2 ^{cd}	2.18	
	Before cropping	4.75 ^b	--	--	--	--	--	--	--	--	

Values within each column and followed by differing letters are significantly different (p ≤ 0.05).

+ Ratio of plant uptake Ca:Na. Ca:Na ratio data was not subjected to Duncan's new multiple range test for significant differences.

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